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ÉTUDE SUR LA DÉCOMPOSITION THERMIQUE DES PARATUNGSTATES D'AMMONIUM *A* ET *B*

PAR

N. CALU et ŞTEFANIA GAVRILIU

1. Introduction

Dans la technologie de l'obtention des poudres de tungstène il est essentiel de connaître les conditions et le mécanisme de la transformation à chaud des paratungstates d'ammonium en trioxyde de tungstène. Jusqu'à présent les études thermogravimétriques concernant la décomposition dans l'air [1]...[4] et dans le vide [5] des paratungstates d'ammonium ont montré la présence d'une phase intermédiaire, mais n'ont pas fait la différence et n'ont pas saisi des différences concernant le comportement parmis les différents anions paratungsténiques dont l'existence est unanimement reconnue [6]...[11].

Pour obtenir des polytungstates, un rôle important [6]...[11] jouent le pH et la concentration, aussi que le temps et la température. Dans les solutions de polytungstates obtenues par acidulage des tungstates autour de pH = 6, on peut distinguer deux types de paratungstates, notés d'habitude par paratungstate *A* et paratungstate *B* (ou *Z*). Le paratungstate *A*, avec une structure peu connue, passe lentement sous la forme *B* avec l'anion $H_2W_{12}O_{42}^{10-}$. Ainsi, à chaud, les propriétés des solutions fraichement préparées de paratungstate *A* se modifient grâce à la formation et au déplacement des équilibres vers le paratungstate *B*.

Dans ce qui suit on donne les résultats des recherches concernant la décomposition thermique dans l'air des paratungstates d'ammonium de type *A* et *B*.

2. Partie expériementale

2.1. Le paratungstate d'ammonium *A*

La forme *A* de paratungstate a été obtenue par dissolution de l'acide tungsténique dans l'ammoniaque à la température ambiante et par ajustage du pH de la solution autour de la valeur 6,9. Les cristaux séparés ont été séchés sous vide.

2.2. Le paratungstate d'ammonium *B*

La forme *B* de paratungstate a été obtenue d'une solution concentrée par les anions de paratungstate *A*, comme ci-dessus, par bouillonnement pendant 20 heures. Les cristaux séparés ont été séchés sous vide [12].

La composition chimique de ces deux types de paratungstates d'ammonium est donnée dans le Tableau 1.

L'étude thermogravimetrique de la décomposition des deux paratungstates d'ammonium *A* et *B* a été effectuée dans des conditions dynamiques et isothermes—isobares.

Les produits de réaction dans les différentes étapes du calcinage de ces composés ont été analysés par voie chimique et cristalochimique.

Pour la derivatographie thermique on a utilisé un dérivatographe système F. Paulik— J. Paulik—L. Erdey, M.O.M. Budapest.

Tableau 1

La composition des paratungstates d'ammonium A et B

Le composé	Composition chimique	WO_3 %		$NH_3 + H_2O$ %	
		calculé	expérimental	calculé	expérimental
Paratungstate d'ammonium *A*	$(NH_4)_{10}W_{12}O_{41} \cdot 11H_2O$	85,81	86,14	14,19	13,86
Paratungstate d'ammonium *B*	$(NH_4)_{10}W_{12}O_{41} \cdot 5H_2O$	88,81	89,25	11,19	10,75

3. Résultats et Dissecusions

3.1. La décomposition thermique des paratungstates d'ammonium *A* et *B*

Le comportement à chaud de ces deux paratungstates d'ammonium a été étudiée par dérivatographie thermique (Fig. 1.).

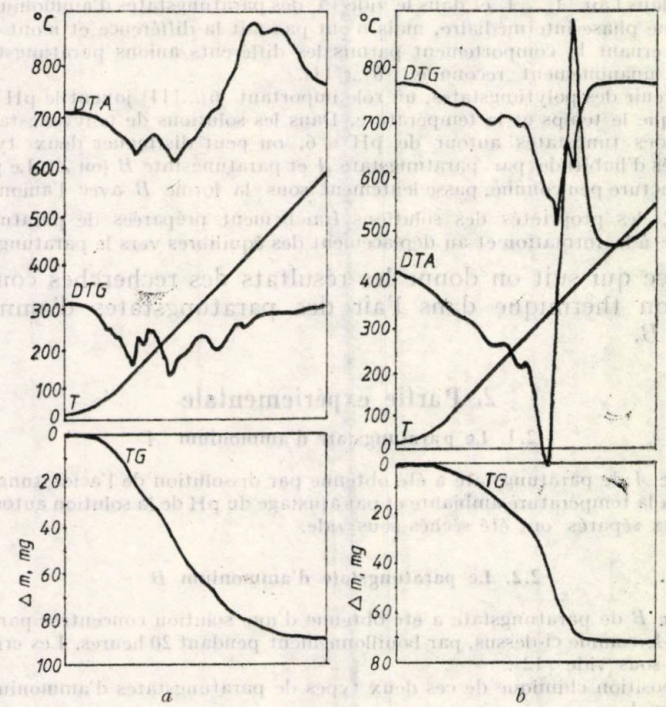


Fig. 1. — Les dérivatogrammes enregistrées à la décomposition dans l'air des deux paratungstates d'ammonium : *a* — le paratungstate d'ammonium *A* (pwa *A*) ; *b* — le paratungstate d'ammonium *B* (pwa *B*) ; la vitesse de chauffage, 10°C/min. ; la sensibilité DTA 1/10 ; la sensibilité DTG 1/15 ; la masse de l'épreuve, pwa *A* — 620 mg, pwa *B* — 640 mg.

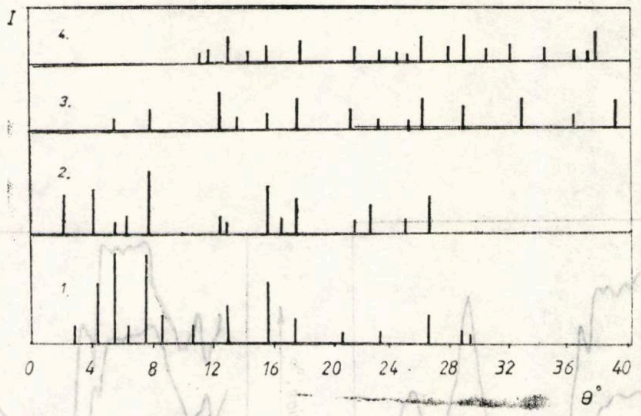


Fig. 2.—Les Roentgenogrammes enregistrées pour le paratungstate d'ammonium *A* (pwa *A*) et les produits des différentes étapes de décomposition thermique : *1* — pwa *A* ; *2* —pwa *A* à 180°C ; *3* — pwa *A* à 260°C ; *4* — pwa *A* à 520°C (coïncident avec celles obtenues pour WO_3).

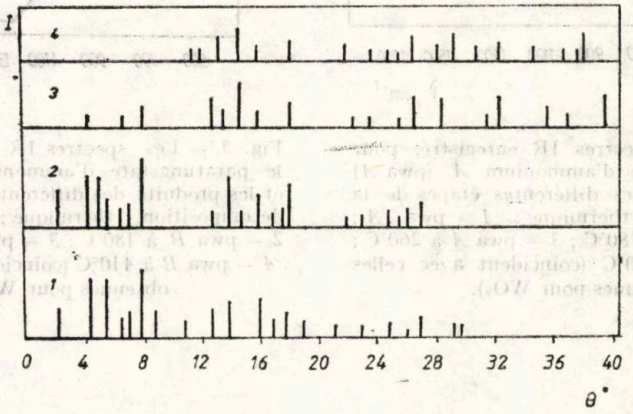


Fig. 3.—Les Roentgenogrammes enregistrées pour le paratungstate d'ammonium *B* (pwa *B*) et les produits des différentes étapes de décomposition thermique : *1* — pwa *B* ; *2* — pwa *B* à 180°C ; *3* — pwa *B* à 260°C ; *4* — pwa *B* à 410°C (coïncident avec celles obtenues pour WO_3).

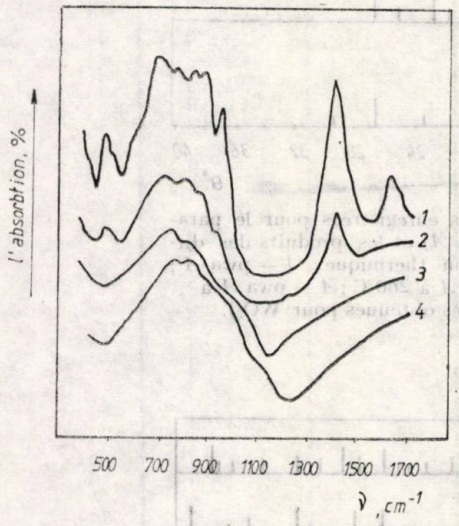


Fig. 4. — Les spectres IR enregistrés pour le paratungstate d'ammonium *A* (pwa *A*) et les produits des différentes étapes de la décomposition thermique : *1* — pwa *A* ; *2* — pwa *A* à 180°C ; *3* — pwa *A* à 260°C ; *4* — pwa *A* à 520°C (coïncident avec celles obtenues pour WO_3).

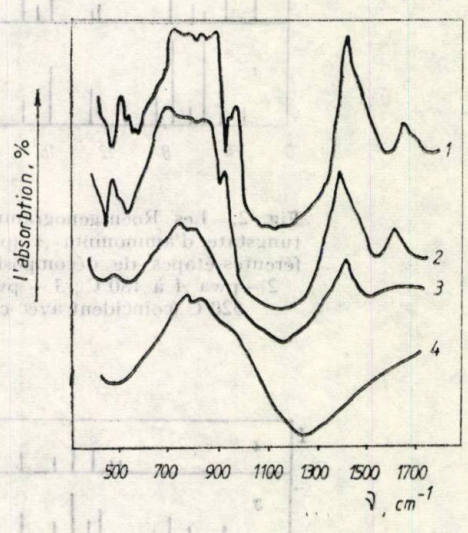


Fig. 5. — Les spectres IR enregistrés pour le paratungstate d'ammonium *B* (pwa *B*) et les produits des différentes étapes de la décomposition thermique ; *1* — pwa *B* ; *2* — pwa *B* à 180°C ; *3* — pwa *B* à 260°C ; *4* — pwa *B* à 410°C (coïncident avec celles obtenues pour WO_3).

Ensuite, par chauffage des composés initials, dans un four, à des températures qui correspondent aux ces étapes, on a obtenu une série de produits intermédiaires aussi bien que des produits finaux. À l'analyse de ceux-ci par rayons X, spectroscopie IR et chimique (Fig. 2 ... 5), en comparant avec les données obtenues pour une probe étalon de trioxyde de tungstène, on a établi les formes obtenues au décomposition des deux paratungstates d'ammonium (*A* et *B*).

À l'aide des données expérimentales obtenues (Fig. 1 ... 5) on a abouti aux conclusions suivantes :

a) Les formes des courbes thermogravimetriques et thermodifférentielles enregistrées dans les même conditions pour les deux paratungstates d'ammonium diffèrent entre elles.

b) Les effets thermiques vers 100°C, mis en évidence sur les courbes DTA, sont plus grands au paratungstate d'ammonium *A* qu'au paratungstate d'ammonium *B*, grâce a l'élimination chez la premier d'une plus grande quantité d'eau libre.

c) La décomposition thermique des deux paratungstates d'ammonium (*A* et *B*) présente d'une façon essentielle la même évolution (en différant seulement par l'intervalle de températures dans le quel ont lieu les transformations et par la composition des produits intermédiaires), l'élimination partielle de l'eau libre (qui ne participe pas à la formation de la réseau cristalline) de l'ammoniaque, de l'eau de constitution (qui participe à la formation de la réseau cristalline) et de l'ammoniaque.

d) Les transformations structurelles commencent dans l'intervalle de températures 160° ... 200°C avec la constitution des bronzes d'ammonium amorphes.

e) La constitution des bronzes cristallines, commençant à 250°C, pour les deux formes de paratungstate d'ammonium, est marquée par l'apparition de quelques inflexions sur les courbes thermogravimétriques.

f) Le trioxyde de tungstène apparaît comme une impureté dans les bronzes de tungstène pour les deux paratungstates, dans l'intervalle de températures de 300° ... 350°C.

g) Les températures des effets thermiques et thermogravimétriques enregistrés sur les courbes thermodifférentielles, aux différentes vitesses de chauffage du four, sont déplacées vers des valeurs plus élevées, en même temps que l'augmentation de la vitesse de chauffage du four, comme on peut observer dans le Tableau 2.

h) Les formes des courbes dérivatographiques ne diffèrent pas, dans certaines limites, de la dispersion du paratungstate initiel et de la vitesse de chauffage.

Plus précisément, les deux paratungstates d'ammonium ont pour effet les suivantes transformations de décomposition, en fonction de la température :

a) le paratungstate d'ammonium *A* :

$$5(NH_4)_2O \cdot 12WO_3 \cdot 11H_2O \xrightarrow{100°C} 5(NH_4)_2O \cdot 12WO_3 \cdot 9H_2O \xrightarrow{100°...200°C}$$

$$\xrightarrow{100°...200°C} 4{,}5(NH_4)_2O \cdot 12WO_3 \cdot 9H_2O \xrightarrow{200°...280°C} 3{,}5(NH_4)_2O \cdot 12WO_3 \cdot 5H_2O \xrightarrow{280°...335°C}$$

Tableau 2

Le déplacement des effets thermogravimétriques à décomposition dans l'air, dans des conditions dynamiques, des paratungstates d'ammonium A et B, en fonction de la vitesse de chauffage du four

La vitese de chauffage du four °C/min	Les températures des effets thermogravimetriques, [°C]		
	Le commencement de la réaction	Les vitesses maximum de la réaction	Le fin de la réaction
Le paratungstate d'ammonium *A*			
2,5	58	135 ; 225 ; 300 ; 330 ; 405	515
5	60	135 ; 228 ; 312 ; 335 ; 410	518
10	65	138 ; 232 ; 320 ; 343 ; 416	520
Le paratungstate d'ammonium *B*			
2,5	64	98 ; 178 ; 252 ; 300	405
5	70	100 ; 180 ; 255 ; 310	410
10	75	110 ; 205 ; 260 ; 320	410

$$\xrightarrow{280°...335°C} \rightarrow 1{,}5(NH_4)_2O_3 \cdot 12WO \cdot 3H_2O \xrightarrow{335°...450°C} \rightarrow$$

$$\xrightarrow{335°...450°C} \rightarrow 0{,}5(NH_4)_2O \cdot 12WO_3 \cdot 0{,}5H_2O \xrightarrow{450°...520°C} \rightarrow 12WO_3,$$

b) le paratungstate d'ammonium *B* :

$$5(NH_4)_2O \cdot 12WO_3 \cdot 5H_2O \xrightarrow{60°...100°C} \rightarrow 5(NH_4)_2O \cdot 12WO_3 \cdot 4H_2O \xrightarrow{160°..180°C} \rightarrow$$

$$\xrightarrow{160°..180°C} \rightarrow 4(NH_4)_2O \cdot 12WO_3 \cdot 4H_2O \xrightarrow{180°...260°C} \rightarrow$$

$$\xrightarrow{180°...260°C} \rightarrow 3(NH_4)_2O \cdot 12WO_3 \cdot 4H_2O \xrightarrow{260°...310°C} \rightarrow$$

$$\xrightarrow{260°...310°C} \rightarrow 0{,}5(NH_4)_2O \cdot 12WO_3 \cdot 0{,}75H_2O \xrightarrow{410°C} \rightarrow 12WO_3.$$

À l'aide d'un microscope on observe les suivantes transformations dans le processus de décomposition thermiques des deux paratungstates d'ammonium *A* et *B* :

a) la couleur du paratungstate d'ammonium *A*, calciné dans l'air, passe de blanc transparent (20° ... 100°C) au blanc opaque (100° ... 280°C), blanc-gris, blanc-jaune (300°...320°C), jaune-orange, jaune-pâle (340° ... 500°C),

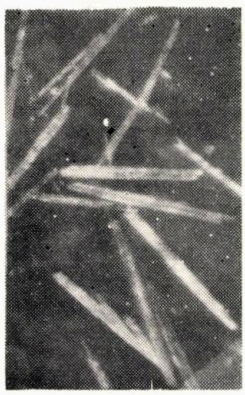
b) la couleur du paratungstate d'ammonium *B*, calciné dans l'air, passe de blanc transparent (20° ... 80°C) au blanc-opaque (80° ... 280°C), blanc-jaune (280° ... 300°C), rouge-brun (310°C), jaune-pâle (410°C) ;

c) si l'ammoniaque n'est pas éliminé d'une façon inintérrompue de l'enceinte de réaction par un courant d'air, il réduit partiellement le trioxyde de tungstène et la couleur du produit final est jaune-verte ;

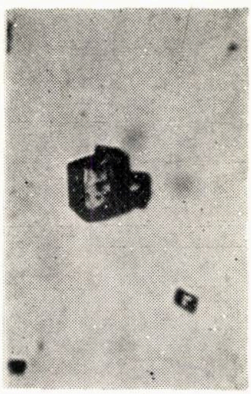
d) les bronzes de tungstène résultés dans ces processus de décomposition ont une composition et une couleur qui varient en fonction de la température et les conditions de travail.

À la fin de la décomposition thermique des deux paratungstates (*A* et *B* — Fig. 6), on constate que :

a) la forme et les dimensions des grains ne subissent pas de grandes variations pendant le processus de décomposition ;



a

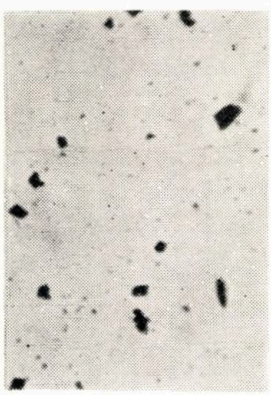


a'

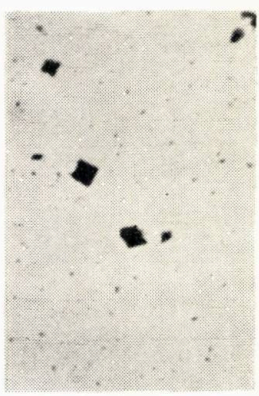
b

b'

c



d



d'

Fig. 6. — La transformation des cristaux pendant la décomposition thermique dans l'air des paratungstates d'ammonium *A* (pwa *A*) et *B* (pwa *B*): *a*—cristaux aciculairs de pwa *A* à 20°C ; *b* — pwa *A* à 160°C ; *c* — pwa *A* à 200°C ; *d*—pwa *A* à 520°C (pratiquement des cristaux de WO_3) ; *a'*—cristaux aplatis rhombiques de pwa *B* à 20°C ; *b'*—pwa *B* à 160°C ; *d'*— pwa *B* à 410°C (pratiquement des cristaux de WO_3).

b) la destruction des cristaux commence de l'intérieur vers l'extérieur, ainsi que les coins et les arêtes restent généralement stables, en permettant la soudure des petites particules.

Toutefois, par l'étude des transformations cristallochimiques on a constaté que tant le paratungstate d'ammonium *A* (initiallement sous la forme des aiguilles longues, cristallisées dans le système orthorombique, la classe mmm), que le paratungstate d'ammonium *B* (initiallement sous la forme des cristaux plats rhombique, cristallisées dans le système monoclinique, la classe 2/m), lors de la décomposition thermique dans l'air, dans l'intervalle 200° ... 350°C passent aux bronzes d'ammonium avec la structure nonstoéchiométrique (au commencement amorphes, puis cristallisées, dans la symétrie hexagonale) tandis que au dessus de 360°C commence la constitution du trioxyde de tungstène ayant une symétrie orthorombique.

3.2. Les paramètres cinétiques de la décomposition thérmique des paratungstates d'ammonium *A* et *B*

Les calculs des paramètres cinétiques (l'ordre de réaction, l'énergie d'activation et la constate de la vitesse de la réaction) ont été effectués à

Tableau 3

Les paramétres cinétiques de la décomposition thermiques dans l'air des deux paratungstates d'ammonium A et B

La température, t	L'énergie d'activation, E	L'ordre de réaction, n	L'exprèssion de la constante de vitesse de réaction, k	Les produits de décomposition
°C	kcal/mol		min^{-1}	
Paratungstate d'ammonium *A*				
95 ... 138	4,00	1,0	$5,15 \cdot 10^2 \exp(-4,00/RT)$	Paratungstate d'ammonium sans eau de cristallisation.
200 ... 232	22,5	1,5	$5,37 \cdot 10^9 \exp(-22,5/RT)$	Polytungstates avec des structures nondéterminées et bronzes amorphes.
302 ... 320	6,32	2,3	$2,32 \cdot 10 \exp(-6,32/RT)$	Bronzes cristallines.
335 ... 343	106,0	3,5	$3,76 \cdot 10^{35} \exp(-106/RT)$	Bronzes cristallines et WO_3.
405 ... 416	7,02	0,3	$4,08 \cdot 10^4 \exp(-7,02/RT)$	Bronzes cristallines et WO_3.
500 ... 520	93,0	5,2	$2,96 \cdot 10^{23} \exp(-93,0/RT)$	WO_3 et bronzes cristallines.
520	—	—	—	WO_3.
Paratungstate d'ammonium *B*				
75 ... 110	10,6	1,0	$1,51 \cdot 10^6 \exp(-10,6/RT)$	Paratungstate d'ammonium sans eau de cristallisation.
145 ... 187	5,78	1,0	$1,44 \cdot 10^3 \exp(-5,78/RT)$	Polytungstates avec des structures nondéterminées et bronzes amorphes.
250 ... 260	7,04	4,25	$2 \cdot 10^{-2} \exp(-4,25/RT)$	Bronzes amorphes et bronzes cristallines.
280 ... 358	23,0	1,05	$9,99 \cdot 10^{37} \exp(-23/RT)$	Bronzes cristallines.
382 ... 400	52,0	3,06	$3,98 \cdot 10^{17} \exp(-52/RT)$	Bronzes cristallines et WO_3.
410	—			WO_3.

l'aide des dérivatogrammes présentées dans la Fig. 1, par la méthode de Freeman-Carroll [13]. Les résultats sont présentés dans le Tableau 3.

La variation du degré de transformation, en fonction de la température, pour le paratungstate d'ammonium *A*, respectivement le paratungstate d'ammonium *B*, a été presentée dans les Fig. 7 et 8.

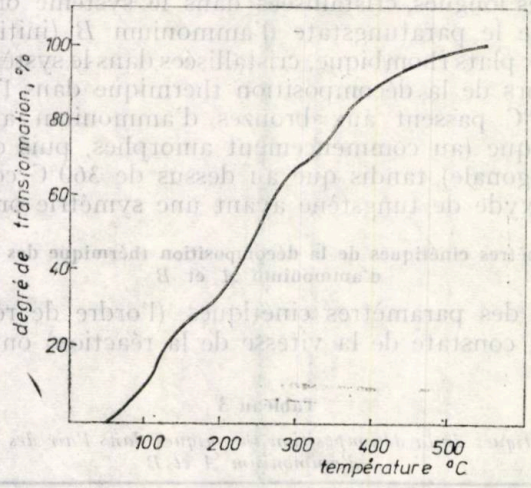


Fig. 7. — La variation du degré de transformation, en fonction de la température, lors de la décomposition du paratungstate d'ammonium *A*.

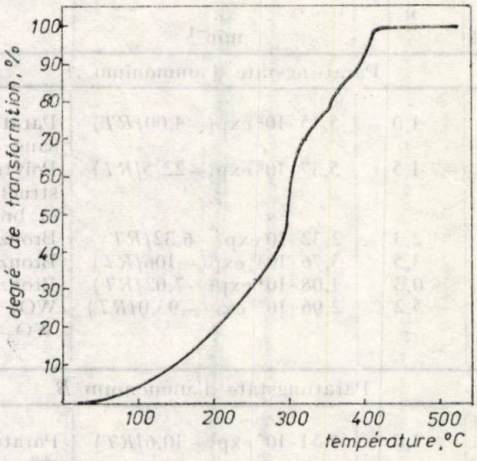


Fig. 8. — La variation du degré de transformation, en fonction de la température, lors de la décomposition du paratungstate d'ammonium *B*.

Outre les données du Tableau 3 on peut mentionner encore que:

a) dans la période initielle de la calcination, jusqu'a 160°C, l'eau qui ne participe pas à la constitution du réseau est éliminée dans le régime cinétique, avec des faibles énergies d'activation ;

b) sur la courbe TG, pour le paratungstate d'ammonium *A*, cette première période implique une perte de masse qui correspond à deux molécules d'eau pour un anion de paratungstate, tandis que pour le paratungstate d'ammonium *B*, la perte de masse correspond à une seule molécule d'eau pour un anion de paratungstate ;

c) en même temps que le dégagement de l'ammoniaque, à des températures qui dépassent 160°C le régime devient de diffusion et l'énergie d'activation augmente ;

d) la variation des parametrès cinétiques pendant le processus de décomposition en fonction de la température, autant qu'en fonction de la vitesse de chauffage de l'épreuve, montre que le mécanisme est complexe et découle en étapes.

La comparaison des comportements à la calcination de ces deux paratungstates d'ammonium montre qu'il y a des différences du point de vue des compositions initiales et des produits des phases intermédiaires, autant que du point de vue des paramètres cinétiques de la réaction de décomposition.

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STUDIU ASUPRA DESCOMPUNERII TERMICE A PARAWOLFRAMAŢILOR DE AMONIU *A* ŞI *B*

(Rezumat)

S-a studiat, prin derivatografie termică, descompunerea în aer a parawolframaţilor de amoniu *A* şi *B*. Descompunerea are loc în trepte. În jurul temperaturii de 100°C cei doi parawolframaţi pierd apa neparticipantă la reţea, apoi la temperaturi depăşind 160°C pierd amoniacul şi apa de reţea (constituţie). Produşii intermediari şi finali rezultaţi la această descompunere au fost investigaţi prin analize chimice, de raze X, IR şi microscopic. Printre produşii intermediari se află bronzurile de wolfram iar produsul final, rezultat la 520°C, de la forma *A* şi respectiv la 410°C, de la forma *B*, este trioxidul de wolfram. Au fost calculaţi parametrii cinetici ai descompunerii termice. Energia de activare este de 4...10,6 kcal/mol pentru îndepărtarea apei neparticipante la reţea, dar aceasta creşte la 10,6...52,0 kcal/mol la celalalte trepte ale descompunerii termice.

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CHEMICAL EQUILIBRIA OF SODIUM SILICATES IN AQUEOUS MEDIUM

BY

I. ROŞCA and ELENA ŞTEFANCU

1. Generalities about Chemical Equilibria of SiO_2 and some Silicates in Aqueous Medium

The use of soluble silicates, especially of sodium silicate, in numerous fields requires studies on their behaviour toward different chemical compounds.

Numerous paper have been reported on different systems from which a great variety of silicates result in both liquid and solid phases [1]...[5].

The studies on different systems, such as SiO_2-H_2O ; $MO-SiO_2-H_2O$, etc., revealed numerous equilibria between different silicates [1]...[8]. For example, the following kalium silicates appear within the $K_2O-SiO_2-H_2O$ system at temperatures between 200°...600°C ; $K_2O \cdot SiO_2 \cdot H_2O$, $K_2O \cdot SiO_2 \cdot 0.5\,H_2O$, $K_2O \cdot 2SiO_2 \cdot H_2O$, compounds with incongruent solubility, and $K_2O \cdot 4\,SiO_2 \cdot H_2O$, a compound with congruent solubility.

The $K_2O \cdot 2\,SiO_2 \cdot H_2O$ and $K_2O \cdot 4SiO_2 \cdot H_2O$ have incongruent solubilities at the room temperature and the following equilibria are settled ;

$$2(K_2O \cdot 2SiO_2 \cdot H_2O) + n\,H_2O \rightleftarrows K_2O \cdot 4SiO_2 \cdot H_2O + \text{solution},$$

$$K_2O \cdot 4SiO_2 \cdot H_2O + n\,H_2O \rightleftarrows 4SiO_2 + \text{solution}.$$

In both cases a great amount of kalium hydroxyde appears in solution as a consequence of its higher solubility in comparison with the other components and the residue becomes more enriched with SiO_2.

The solubility of numerous natural and synthetic silicates is generally known to be incongruent ; by interaction with water the hydroxydes of alkaline and alkaline-earth metals pass into solution since they are more soluble, while the hydrosilicates enriched with SiO_2 form the solid phase.

All these processes of silicate formation are determined by the participation of several components to a great variety of equilibria.

As a consequence of chemical equilibria of silicates settled in aqueous medium, gelatinous reaction products appear.

For the study of silicate equilibria in aqueous medium the knowing and understanding of factors determining the shifting of these equilibria are particularly important.

It is advisable in these cases to start from simple equilibria, such as those with the SiO_2-H_2O, $M_2O-SiO_2-H_2O$, $MO-SiO_2-H_2O$ systems, and then to study the influence of other components within the proceeding processes.

As known, under normal pressure and temperature, the interaction and solubility of quartz are negligible, while the amorphous silica interacts

more strongly showing a higher solubility wich depends greatly on the partiale size, pH and temperature. The dissolution mechanism involves the hydrolytic scission of the Si—O—Si bonds in SiO_2 with formation of Si—OH groups, either partially or completely within the entire mass, with formation of silicic acids leading theoretically to the *orto*-silicic acid (H_4SiO_4) :

$$\frac{n}{2}-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-+2nH_2O \rightleftarrows nH_4SiO_4$$

Table 1

Solubility of SiO_2 in Function of pH

pH	1	2	3	4	5	6	7.7	10.3	10.6
SiO_2 %	0.014	0.015	0.015	0.013	0.012	0.011	0.010	0.049	0.112

Since the silicic acids H_4SiO_4, among them, have a pronounced tendency to the polycondensation which depend on pH, temperature and concentration, it is practically imposible to obtain and to keep longer a certain silicic acid.

For instance, the polycondensation of *ortho*-silicic acid proceeds energetically within the 5 ... 6 pH range, while in alkaline medium (pH > 10) it does not practically take place. As mentioned in the paper [14], the polymerization of *ortho*-silicic acid proceeds at a maximum rate at pH = 9 in the presence of $Fe(OH)_3$. Since the silicic acids are very weak, the silicates of alkaline metals, especially sodium silicates, would strongly hydrolyse. The hydrolysis products are of various structures, often rather complicated and difficult for study.

The hydrolysis processes are also complicated by the presence of other components, such as different oxides and hydroxydes (NaOH, KOH, $Ca(OH)_2$, $Fe(OH)_3$, $Al(OH)_3$, etc.), in the aqueous medium.

The hydrolysis of sodium metasilicate proceed as follows :

$$2nNa^+ + (SiO_3^{2-})_n + nH_2O \rightleftarrows nNa^+ + (HSiO_3^-)_n + n(Na^+ + OH^-),$$

$$nNa^+ + (HSiO_3^-)_n + nH_2O \rightleftarrows (H_2SiO_3)_n + n(Na^+ + OH^-),$$

$$(H_2SiO_3)_n + nH_2O \rightleftarrows nH_4SiO_4,$$

$$H_4SiO_4 \rightleftarrows H_3SiO_4^- + H^+,\ K_1 = 10^{-10};\quad H_3SiO_4^- \rightleftarrows H_2SiO_4^{2-} + H^+,\ K_2 = 10^{-12}.$$

Since the study on the processes proceeding with silicates in water are rather difficult, some literature data are contradictory. For instance, some authors [6], [7] consider the silicates within the $CaO—SiO_2—H_2O$ system at 30°C to be salts of *ortho*-silicic acid : $Ca_2SiO_4 \cdot nH_2O$, $Ca_3(HSiO_4)_2 \cdot nH_2O$, $Ca(H_2SiO_4) \cdot nH_2O$, $Ca(H_3SiO_4)_2 \cdot nH_2O$.

B e r n a l [8] has performed Roentgen studies and did not confirme this structure.

The following hydrosilicates are mentioned as resulting from the $CaO-SiO_2-H_2O$ system : $2CaO \cdot SiO_2 \cdot H_2O$, $3CaO \cdot 2SiO_2 \cdot 3H_2O$, with incongruent solubility and $CaO \cdot SiO_2 \cdot 2H_2O$ with congruent solubility, all these compounds being in equilibrium with the liquid phase [1].

Other systems, such as $MgO-SiO_2-H_2O$, $SrO-SiO_2-H_2O$, $BaO-SiO_2-H_2O$, $Na_2O-Fe_2O_3-SiO_2-H_2O$, etc., are rather few studied.

2. Interaction of Sodium Silicates with Different Reagents in Aqueous Medium

As known, the sodium silicates are classified according to the SiO_2 : : Na_2O mole ratio which also determines certain properties. The numerous methods of obtaining sodium silicates may be applied either by dry reactions or in aqueous medium.

The following silicates are particularly important for being used in different fields: sodium metasilicate (50% Na_2O, 0.48% SiO_2), whose pH for a 1% solution is 12.6, sodium silicate of SE type (7.8% Na_2O ; 24% SiO_2) manufactured in great ammounts in our country.

The sodium metasilicate can be obtained by several methods, among which those described in the patents [9] ... [12] corresponding to the formula Na_2SiO_3 are quite important.

The structure of sodium silicate anions is various and may be represented by the principal structural types *I* ... *III*.

Other structures of sodium silicates are also known and they may be considered as including partially some of the above mentioned structures.

In the following, the equilibrium of sodium silicates with water, strong and weak acids, sodium hydroxyde and some salts will be discussed.

All sodium silicates strongly hydrolyse, this equilibrium process depending on concentration, temperature and pH.

Due to the hydrolsyis, the aqueous solutions of sodium silicates show a high pH value. A 0.08 M Na_2SiO_3 solution, for instance, has pH = 12.7, as measured experimentally.

By acidifying the sodium silicates solutions, silicic acids are obtained as colloidal solutions, at low concentrations, or as gels, at high concentrations, corresponding to the hydrated silicium dioxide.

The colloidal particles correspond to the formula :

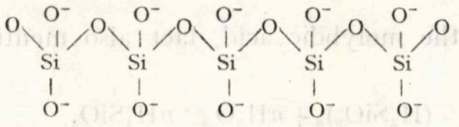
$$[(SiO_2)_n \cdot m SiO_3^{2-}]^{2m-} \text{ or } [(SiO_2)_n \cdot m SiO_3^{2-} \cdot 2(m-x)Na^+]^{2x-}.$$

The polysilicic acids may be depolymerised in the presence of molybdic acid which is also used for determining the content of soluble SiO_2 in silicium sols.

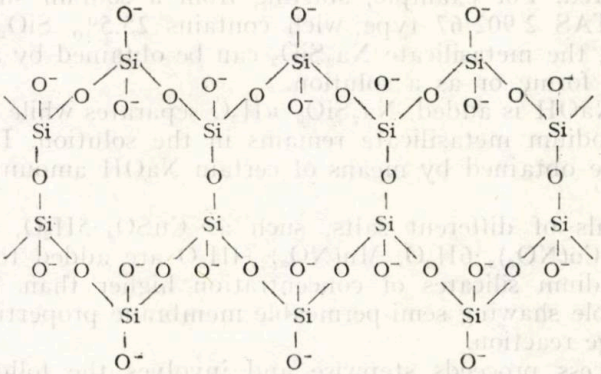
The reaction rate depends on the particle size and the Si—OH group content or on the percentage of sodium silicates non hydrolysed completely.

When the particle size is larger than 20 mμ, the reaction of polysilicic acids with molybdic acid is negligible.

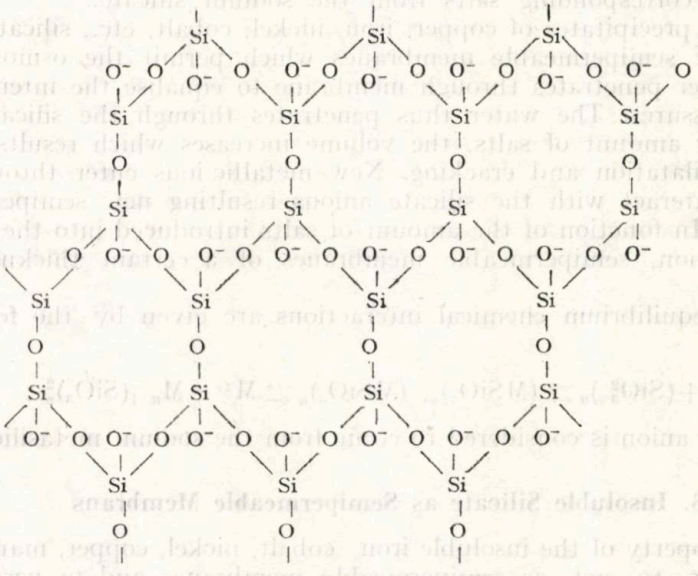
In case of very small particles the formation of silicomolybdic acid was found to proceed at a constant rate, through depolymerization of



Structural type *I* for $(SiO_3^{2-})_n$; $Na_2O \cdot SiO_2$; Na_2SiO_3.



Structural type *II* for $Si_4O_{11}^{6-}$; $3\,Na_2O \cdot 4\,SiO_2$.



Structural type *III* for $(Si_2O_5^{2-})_n$; $Na_2O \cdot 2\,SiO_2$.

polysilicic acids by the molybdic acid, fact also mentioned in literature [13] :

$$(H_2SiO_3)_n + nH_2O \rightleftarrows nH_4SiO_4,$$

$$H_4SiO_4 + 12H_2MoO_4 \rightleftarrows H_4[SiMo_{12}O_{40})] + 12H_2O.$$

By adding Na_2O or NaOH to the solutions of sodium silicates with the modul $SiO_2 : Na_2O > 1$, silicates of well-defined structure can be obtained as desired. For example, starting from a sodium silicate solution of the SE, STAS 2 902/67 type, wich contains 25.5% SiO_2, 8.3% Na_2O and 66% H_2O, the metasilicate Na_2SiO_3 can be obtained by adding NaOH either in solid forme or as a solution.

If solid NaOH is added, $Na_2SiO_3 \cdot nH_2O$ separates while with a NaOH solution the sodium metasilicate remains in the solution. In both cases, Na_2SiO_3 can be obtained by means of certain NaOH amount resulting by calculation.

If crystals of different salts, such as $CuSO_4 \cdot 5H_2O$, $FeSO_4 \cdot 7H_2O$, $NiSO_4 \cdot 7H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Mn(NO_3)_2 \cdot 4H_2O$ are added to the aqueous solution of sodium silicates of concentration higher than 10%, silicates sparingly soluble shawing semi-permeable membrane properties are formed by an exchange reaction.

The process proceeds stepwise and involves the following stages :

1. Passing of the ions from the crystall into the aqueous medium. This process proceeds slowly due to the formation of concentrated salt solution around the crystals.

2. Interaction of the metal ions with the anions coming from the sodium silicate and the formation of insoluble silicate as a membrane separating the corresponding salts from the sodium silicate.

3. The precipitates of copper, iron, nickel, cobalt, etc., silicates show properties of semipermeable membranes which permit the osmosis ; the external water penetrates through membrane to equalise the internal and external pressures. The water thus penetrates through the silicates and solves a new amount of salts, the volume increases which results in the membrane dilatation and cracking. New metallic ions enter through the crack and interact with the silicate anions resulting new semipermeable membranes. In fonction of the amount of salts introduced into the sodium silicate solution, semipermeable membranes of a certain thickness are obtained.

These equilibrium chemical interactions are given by the following equations :

$$nM^{2+} + (SiO_3^{2-})_n \rightleftarrows (MSiO_3)_n, \quad (MSiO_3)_n \rightleftarrows M^{2+} + M_{n-1}(SiO_3)_n^{2-},$$

if the silicate anion is considered to come from the sodium metasilicate.

3. Insoluble Silicate as Semipermeable Membrans

The property of the insoluble iron, cobalt, nickel, copper, manganese, etc., silicates to act as semipermeable membranes and to permit the passing of water only was used for determining the soil humidity.

With this purpose, a cylinder of 4 cm length and 3 cm diameter was made in calcined gypsum and two concentric electrodes of sieve of stainless steel placed inside at a distance of 1 cm one from the other. This cylinder was introduced into the solution of iron, cobalt, nickel, cooper, manganese, etc., salt and then dried. After drying it was introduced into a 10% sodium metasilicate solution. Thus, insoluble iron, nickel, cobalt, copper, manganese, etc., silicates, formed by an exchange reaction which showed properties of a semipermeable membrane. The cylinder thus prepared is introduced into soils of known variable humidity and the electric resistance measured by means of a source of alternating current of 2 ... 3 000 Hz. A standard curvei s then drawn in the soil humidity—electrical resistance coordinates (Fig. 1).

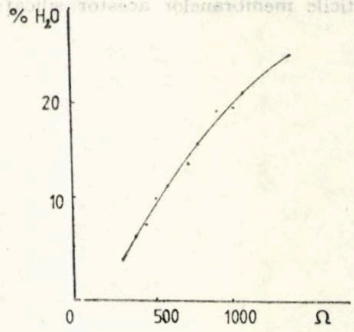


Fig. 1. — Standard curve: electrical resistance vs. soil humidity.

The soil humidity is determined by measuring the electrical resistance by means of which the corresponding humidity value is taken from the standard curve. Under these, the errors are of 1 ... 5%.

The best results were obtained with a cylinder made in a very porous material. This could be done by adding ground glass (3 ... 5%) and plastic powder (3 ... 5%) to the initial calcined gypsum.

This equipment is quite usefull in determining the soil humidity for maintaining a certain fertility regime.

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ECHILIBRE CHIMICE, ÎN MEDIU APOS, ALE SILICAȚILOR DE SODIU

(Rezumat)

Procesul de formare a silicaților de sodiu și a altor silicați în apă a făcut obiectul de studiu a numeroase cercetări, totuși, în literatură, pînă în prezent, nu sînt suficiente date cu privire la folosirea silicaților de sodiu și a altor cationi pentru obținerea membranelor permeabile.

S-au cercetat echilibrul silicaților de natriu și altor cationi (Cu(II), Mn(II), Fe(II), Fe(III), Co(II) și Ni(II)) în apă pentru obținerea membranelor permeabile. Sînt prezentate caracteristicile membranelor acestor silicați în apă.

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THE DETERMINATION OF THE SOLUBILITY PRODUCT FOR SOME HEXANITROCOBALTIATS USING THE CONDUCTOMETRICAL WAY

BY

LUMINIŢA PĂUNESCU, ISTVAN VERESS and VICTOR NĂNESCU

1. Introduction

The solubility product is a very important constant in anorganical and analytical chemistry. Hexanitrocobaltiats are, generally, dificult soluble, exceptions beeing rare (the barium hexanitrocobaltiat is soluble in water, forming an orange solution). Knowing the large application of these salts in analytical field, we consider important to determine the solubility product of hexanitrocobaltiats and we decided on the potasium one. For this purpose we have used the classical way and also the conductometrical studies.

2. Experimental

$K_3[Co(NO_2)_6]$ Chemical Lacherna n.p. Brno ; $Na_3[Co(NO_2)_6]$ p.a. ; H_2SO_4 p.a. were used.

2.1. Classical Chemical Analysis [1], [2]

The potassium salt (in powder) was covered with water and intermittently agitated for eight houres. It was decanted and filtered through blue filter paper. Then, the filtrate was complete evaporated on water bath. The product was cooled and weighted. Before that, we have done the verification of non composition of $K_3[Co(NO_2)_6]$ at bath temperature.

The product obtained at complete evaporation was treated with H_2SO_4 on the sieve, calcinated and weighted. It was considered to be made of cobalt and potassium sulphats (this is verified) :

$$2K_3[Co(NO_2)_6]+5H_2SO_4=3K_2SO_4+2CoSo_4+10HNO_2+2NO_2.$$

The potassium and cobalt ions concentrations were calculated. The results are presented in Table 1.

The solubility product obtained at 20°C has the value :

$$P_s=(1.9795\pm0.0465)\times10^{-14}.$$

2.2. Conductometrical Analysis

The solubility determination of difficult soluble substances on conductometrical way has the advantage of using the possibility of a very

good measurement for little conductibilities. The method is accurately exact if very pure water is employed. We used the bidistilled water.

Table 1

Classical Chemical Analysis

I. 0.1296 g $K_3[Co(NO_2)_6]$ after evaporation

$$\downarrow$$

$$0.03350 \text{ g } K^+ + 0.09600 \text{ g } [Co(NO_2)]^{3-};$$

$$E_{K^+} = 39\ ;\ E_{[Co(NO_2)_6]^{3-}} = 111{,}6\ ;$$

$$C = 0.00086 = \frac{0.03350}{39} = \frac{0.09600}{111{,}6}\ ;$$

$$P_s = 2.026 \times 10^{-14}.$$

II. 0.1179 g $K_3[Co(NO_2)_6]$ after H_2SO_4 addition and calcination, then :

$$m_{3K_2SO_4+2CoSO_4} = 0.1179\ ;$$

$$\downarrow$$

$$0.03315 \text{ g } K^+ + 0.09486 \text{ g } [Co(NO_2)_6]^{3-};$$

$$C = 0.00085 = \frac{0.03315}{39} = \frac{0.09486}{111{,}6}\ ;$$

$$P_s = 1.933 \times 10^{-14}\ ;$$

$$P_{s\,\text{total}} = 1.9795 \times 10^{-14}.$$

Difficult soluble substances can be considered, in first approximation, totally dissociated. Accordingly, their equivalent conductibility is the same with the limit value, these conductibilities being calculated through addition way from the known mobilities of the considered ions.

The mobility of $[Co(NO_2)_6]^{3-}$ must be known. For this purpose $Na_3[Co(NO_2)_6]$ was used in solutions of varying concentrations (N/5 ... N/10 000). The resistance was determined for several cases with a K o h l r a u s c h catwalk, using three temperatures. The obtained data were analysed employing the well known relations :

$$\frac{1}{R} = \lambda_{det},\quad \lambda_{ef} = \lambda_{det} - \lambda_{water},\quad \text{(s. Table 2)},$$

$$\lambda_{et}\theta = \frac{1}{1000}\sum_i c_i\lambda_i = \lambda_0\ [3],$$

where $\theta = 0.6494$ — cell constant (determined with KCl solutions).

The relation can be written because (and this was mentioned yet at time) the equivalent conductibility for the difficult soluble salts is identical with the equivalent conductibility at infinit dilution :

$$\Lambda_m = \frac{1000\Lambda_0}{c}.$$

The obtained results are related in Table 3.

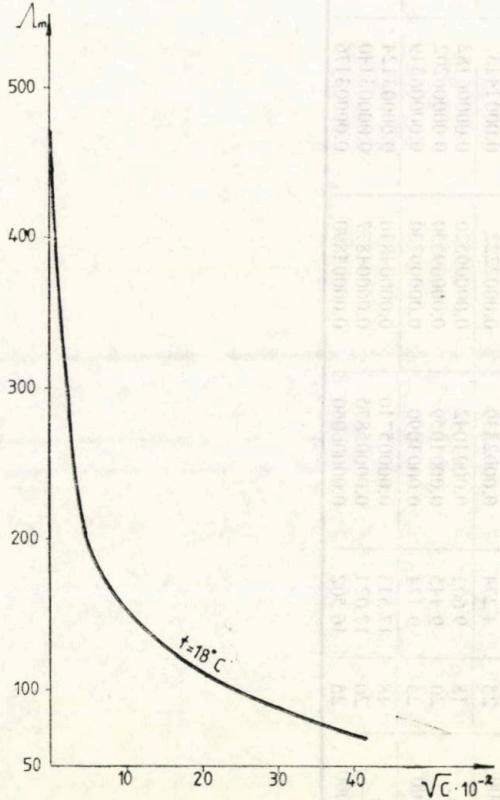

Fig. 1. — Λ_m vs. $\sqrt{c} \times 10^{-2}$ at 18°C.

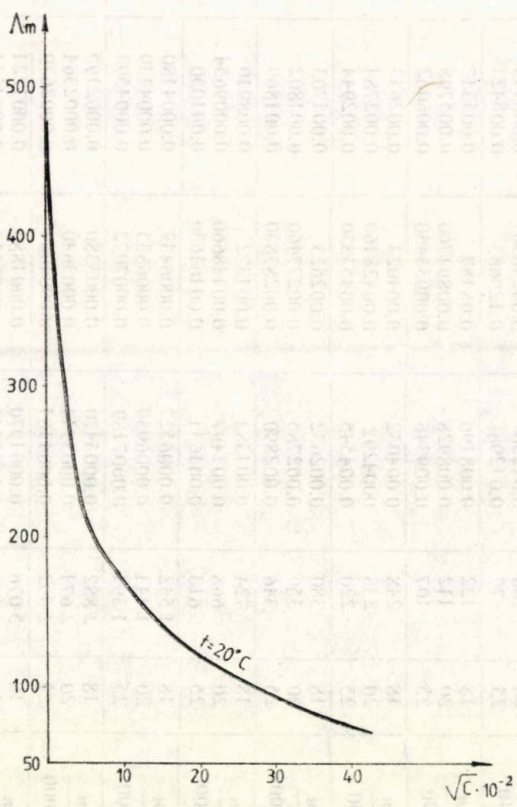

Fig. 2. — Λ_m vs. $\sqrt{c} \times 10^{-2}$ at 20°C.

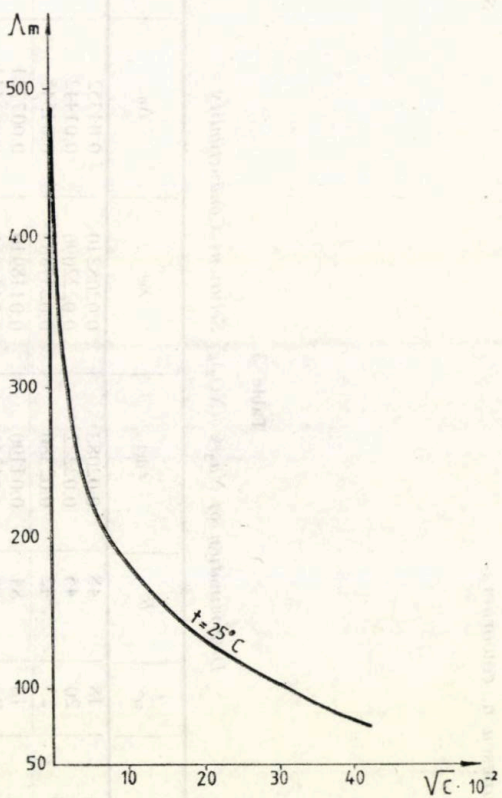

Fig. 3. — Λ_m vs. $\sqrt{c} \times 10^{-2}$ at 25°C.

Table 3

Determination of $Na_3[Co(NO_2)_6]$ Solutions Conductibility

c	t °C	R	λ_{det}	λ_{ef}	Λ_0	Λ_m
$\frac{n}{5}$	18	48	0.02083	0.0208210	0.01352	67.60
	20	45	0.02222	0.0222096	0.01442	72.00
	25	42	0.02380	0.0237883	0.01545	77.25
$\frac{n}{10}$	18	84	0.01190	0.0118910	0.007721	77.21
	20	80	0.01250	0.0124896	0.008111	81.11
	25	77	0.01298	0.129683	0.008421	84.21
$\frac{n}{20}$	18	122	0.008196	0.08187	0.005317	106.34
	20	112	0.008928	0.00891760	0.005798	115.82
	25	107	0.009346	0.00933430	0.006062	121.22
$\frac{n}{50}$	18	248	0.004032	0.004023	0.002613	130.65
	20	233	0004292	0.00428160	0.002781	139.05
	25	220	0.004545	0.00453330	0.002944	147.20
$\frac{n}{100}$	18	380	0.002632	0.002623	0.001703	170.34
	20	359	0.002785	0.00277460	0.001802	180.20
	25	346	0.002890	0.00287830	0.001869	186.92
$\frac{n}{200}$	18	724	0.001381	0.001372	0.008910	178.20
	20	668	0.001497	0.00148660	0.0009654	193.08
	25	613	0.001631	0.00161630	0.001050	210.00
$\frac{n}{500}$	18	1 532	0.0006527	0.0006437	0.0004180	209.00
	20	1 441	0.0006939	0.0006835	0.0004439	221.95
	25	1 391	0.0007189	0.0007072	0.0004593	229.65
$\frac{n}{1000}$	18	2 882	0.0003470	0.0003380	0.0002195	219.50
	20	2 671	0.0003744	0.0003640	0.0002364	236.40
	25	2 392	0.0004181	0.0004064	0.0002639	263.90
$\frac{n}{2000}$	18	5 076	0.0001970	0.0001880	0.0001221	244.20
	20	4 666	0.0002143	0.0002339	0.0001324	264.80
	25	4 274	0.0002339	0.0002222	0.0001443	288.60
$\frac{n}{5000}$	18	9 601	0.0001042	0.00009520	0.00006182	309.10
	20	9 445	0.0001059	0.00009550	0.00006202	310.10
	25	9 174	0.0001090	0.00009730	0.00006319	315.95
$\frac{n}{10\,000}$	18	17 513	0.00005710	0.00004810	0.00003124	312.40
	20	17 021	0.00005875	0.00004877	0.00003140	314.00
	25	16 502	0.00006060	0.00004890	0.00003176	317.60

Table 2

The Conductibility of the Distilled Water

t °C	R	λ
18	111 110	9×10^{-6}
20	96 153	10.4×10^{-6}
25	85 110	11.7×10^{-6}

Representing $\Lambda_m\sqrt{c}\times10^{-2}$ (from Kohlrausch relation, generally considered as $\Lambda=A\sqrt{c}$, [4], [8]) the equivalent conductibility at infinit dilution is obtained. Employing the relation $\Lambda_{equiv}=\Lambda_m/z$, ($z$=valence), for $z>1$ [9], the graphically determined Λ_m is devided by three. Like this, Λ_{equiv}, for $Na_3[Co(NO_2)_6]$, is determined. It represents the total mobility of Na^+ and $[Co(NO_2)_6]^{3-}$·Na^+ mobility is dependent of temperature. We can found this dependance in tables, so we used them in order to determine the $[CO(NO_2)_6]^{3-}$ mobility [10] (Figs. 1 ...3).

After that we have also determined R for $K_3[Co(NO_2)_6]$. The processing of the data is the same (Table 4). Knowing the $[Co(NO_2)_6]^{3-}$ mobility (as determined before) and for K^+ (from the existant tables) we can apply the relation :

$$c=\frac{1\,000\Lambda}{\sum_i \lambda_i}.$$

With the obtained data it is possible to calculate the solubility product (Table 5). Here are the values :

$t=18°C$ $\quad P_s=1.7900\times10^{-14}$;

$t=20°C$ $\quad P_s=2.0927\times10^{-14}$;

$t=25°C$ $\quad P_s=2.3070\times10^{-14}$.

Table 4

The Obtained Values at the Determination of $K_3[Co(NO_2)_6]$ Conductibility

t °C	R	λ_{det}	λ_{ef}	Λ_0
18	4 257	0.0002349	0.0002259	0.0001476
20	4 005	0.0002497	0.0002393	0.0001554
25	3 755	0.0002663	0.0002546	0.0001653

Table 5

Processing of Experimental Conductometric Data

t °C	λ_{Na^+}	λ_{K^+}	$\lambda_{[Co(NO_2)_6]^{3-}}$	Λ_m	$\Lambda_{echiv.}$	c	P_s
18	43.5	64.6	111.16	464	154.66	8.34×10^{-4}	1.790×10^{-14}
20	45.4	67.3	111.93	472	157.33	8.67×10^{-4}	2.093×10^{-14}
25	50.1	73.5	112.57	488	162.66	8.88×10^{-4}	2.307×10^{-14}

We can observe the concordance between the values obtained by classical chemical analysis and the conductometrical ones.

The $[Co(NO_2)_6]^{3-}$ mobility beeing determined, we can calculate the solubility product for various hexanitrocobaltiats and we also perform methods of gravimetrical and conductometrical analysis for some metals.

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DETERMINAREA PRODUSULUI DE SOLUBILITATE AL UNOR HEXANITROCOBALTIAȚI PE CALE CONDUCTOMETRICĂ

(Rezumat)

S-a determinat mobilitatea ionului hexanitrocobaltic $[Co(NO_2)_6]^{3-}$ și de aici, produsul de solubilitate pentru $K_3[Co(NO_2)_6]$, pe cale conductometrică, pentru trei temperaturi deosebite. Valorile astfel obținute sînt concordante cu cele obținute prin analiza chimică clasică.

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DAS ZUR BESTIMMUNG DES NO_3^- IONES NEBEN HALOGENUR IONEN IN HOHEN KONZENTRATIONEN, VERWENDETE CS-3 VIONIT

VON

FLORICICA MATEI, EUGENIA DONIGA und AL. DUCA

1. Einleitung

Wie bekannt, hat die Bestimmung der NO_3^- Ionenkonzentration (als Säure oder Salz) in Anwesenheit der Halogenurionen (I^-, Br^-, Cl^-) — als Säure oder Salz — ständig Probleme aufgewiesen, da die bekannten chemischen Analysenmethoden schwierig und aufwändig sind. Außerdem erfordern sie ein erheblichen Verbrauch an Reaktanten, die oft schwer zu besorgen sind [1].

In einer vorgehender Arbeit [2] wurde die Anwendungsmöglichkeit der feinfühligen Ion Elektrode studiert die aus verschiedene Membranen mit entsprechender Spezifizität und Trennschärfe zur Dosierung des NO_3^- Ones realisiert wurde [3]...[9].

Die für den NO_3^- Ion hergestellten feinfühlige Ion Elektroden haben als Hauptinterferenzionen die Halogenurionen (I^-, Br^-, Cl^-) daß, auch, aus den Werten der Selektivitätskonstanten ersichtlich ist (Tab. 1).

Tabelle 1

Werte der Selektivitätskonstanten Ki/j (t = 20°C)

j/i	NO_3^-	Br^-	Cl^-
NO_3^-	1	22,82	17,76

In Arbeit [2] wurden bereitst einige der durchgeführten Trennversuche der Interferenzionen beschrieben. Gute Ergebnisse sind mit Ionenaustauscher der Form Ag erzielt worden.

Es wurde in Ag Form umgewandelter Amberlit IR-120 Ionenaustauscher verwendet.

Da die rumänischen Ionenaustäuscher eine hohe Thermostabilität und Festigkeit, sowie ein gutes Verhalten in starke Säure und Alkalilö-

sungen aufweisen, haben wir den Ersatz des Amberlit IR-120 Austauschers mit Vionit CS-3 aus Eigenproduktion versucht.

Die Verwendung einiger Ionenaustauscher stellen das Studiumobjekt mehrerer unserer Arbeiten dar [10], [11].

Die Bestimmung der NO_3^- Ionenspuren erfolgte in Abwässer und in einige Reagenzien. Der Chloridgehalt der analysierten Stoffe ergab 10^{-2} mg/l im Vergleich NO_3^- Ionengehalt von 10^{-4} mg/l. Die Konzentration des NO_3^- Ines wurde mit Hilfe der NO_3^- selektiv Elektrode (LCCA, Cluj-Napoca) ermittelt.

2. Experimentelles Teil

Das Ionenaustauscher Harz wird mit $AgNO_3$ (1 N Lösung) in der Form Silber (Ag) gebracht und anschließend gut mit bidistilliertem Wasser, bis zur kompletten Beseitigung der Ag-Ionen gespüllt.

Weiterhin werden Volumen von je 10 cm^3 Wasser mit einem NO_3^- und Chlorid Ionengehalt zugegeben. Nach einem 2 ... 3 Min. langem Rühren, wird die Lösung in einem Berzeliusbecher übertragen, in dem man anschliessend die flüßige Membrannelektrode, selektives NO_3^- und die Gegenelektrode eintaucht.

Die NO_3^- Ionenkonzentration wird mit Hilfe der Elektrodenfunktion auf Basis der Potentialdifferenz bestimmt.

In Tabelle 2 ist ein Teil, der bei der Bestimmung des NO_3^- Ines neben Chlorid Ionen nach der Trennung auf Vionit CS-3 Austauscher erzielten Ergebnisse, im Vergleich mit Amberlit IR-120 Austauscher dargestellt worden.

Es wurde festgestellt, daß man im Falle dieser Trennung erfolgreich Vionit CS-3 Ionenaustauscher verwenden kann.

Tabelle 2

Daten hinsichtlich der NO_3^- und Cl^- Ionentrennung auf Vionit CS-3 und Amberlit IR-120 Ionenaustauscher

Lot Nr.	$C_{NO_3^-}$ [Ion g/l], nach der Trennung auf	
	Vionit CS-3	Amberlit IR-120
1	$1{,}42 \times 10^{-4}$	$1{,}37 \times 10^{-4}$
2	$1{,}49 \times 10^{-4}$	$1{,}49 \times 10^{-4}$
3	$1{,}78 \times 10^{-4}$	$1{,}75 \times 10^{-4}$
4	$1{,}45 \times 10^{-4}$	$1{,}45 \times 10^{-4}$
5	$1{,}82 \times 10^{-4}$	$1{,}76 \times 10^{-4}$
6	$1{,}44 \times 10^{-4}$	$1{,}48 \times 10^{-4}$

3. Die Reinheitsbestimmung einiger Reagenzien

Wie oben erwähnt wurden Vionit Ionenaustauscher auch zur Bestimmung der NO_3^- Ionenspuren in einige Reagenzien verwendet. Es wurden

Einzelionenspuren in Lithium-Bromid Lösungen die als Entwässerungsmittel in industrielle Kälteanlagen verwendet werden, geprüft.

Zu diesem Zweck wird die Lösung mit 1% izooctilalkohol und $LiNO_3$ (als Korrosionsinhibitor) konditioniert. Die empfohlenen Grenzen für das $LiNO_3$ sind 350 ... 500 ppm, daher die Notwendigkeit einer ständigen Kontrolle des NO_3 Gehaltes in der Lösung.

In der Arbeit [2] wurden die Vorteile der potentiometrischen Bestimmungsmethode mit NO_3^- selektiv Elektrode, im Vergleich mit der von der Herstellungsfirme empfohlene Methode dargestellt, jedoch mit den gleichen Nachteile der Halogenurionen Anwesenheit (diesmal Bromid).

Zur Trennung des NO_3^- Iones vom Bromidion wurden ebenfalls rumänische Ionenaustauscher Vionit CS-3 verwendet.

4. Experimentelles Teil

Aus der 54%-igen Lithium-Bromid Lösung, mit einer Dichte =1,58 g/cm³, wird eine 10^{-1} M Lösung hergestellt. Von dieser Lösung werden 10 ml über das Ionenaustauscher Harz Vionit CS-3 in Ag Form zugegeben, 2 ... 3 Min. gut durchgerührt und anschließend wird in der von den Ionenaustauscher getrennten Lösung die NO_3^- Konzentration potentiometrisch bestimmt.

In Tabelle 3 sind die durch potentiometrischer Bestimmung mit NO_3^- selektiver Membrannelektrode des NO_3^- Iones erzielten Ergebniße dargestellt, nach Rückhaltung des Bromidiones auf Vionit CS-3 im Vergleich mit dessen Rückhaltung auf Amberlit IR-120.

Tabelle 3

Daten betreffend die Trennung des NO_3^- von Br^- auf Vionit CS-3 und Amberlit IR-120

Probe Nr.	$C_{(NO_3^-)}$ [Mol/l], Eingabe	$C_{(NO_3^-)}$ [Mol/l], nach Trennung auf	
		Vionit CS-3	Amberlit R-120
1	1×10^{-4}	$1,08 \times 10^{-4}$	$1,04 \times 10^{-4}$
2	1×10^{-4}	$1,08 \times 10^{-4}$	$1,04 \times 10^{-4}$
3	1×10^{-4}	$1,12 \times 10^{-4}$	$1,08 \times 10^{-4}$
4	1×10^{-4}	$1,08 \times 10^{-4}$	$1,08 \times 10^{-4}$
5	1×10^{-4}	$1,07 \times 10^{-4}$	$1,06 \times 10^{-4}$

5. Schlussfolgerungen

a) Der aus eigener Produktion stammender hochsauerer Ionenaustauscher Vionit CS-3 kann erfolgreich zur Trennung der Anionen (NO_3^- von Halogenur) verwendet werden. In einer vorgehender Arbeit [2] wurde die Anwendungsmöglichkeit der anionaktiven Harze Vionit AT-1 zur Kationtrennung erwähnt.

b) Die aus NO_3^- Violet-kristall in Nitrobenzol hergestellte NO_3^- selektive flüßige Membrannelektrode (LCCA, Cluj-Napoca), kann mit gute Ergebniße zur Bestimmung des NO_3^- Iones in Medien mit hohen Halogenurionengehalt verwendet werden.

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SEPARAREA IMPURITĂŢILOR NO_3^- DIN LiBr UTILIZÎND SCHIMBĂTORI DE IONI VIONIT CS-3

(Rezumat)

Soluţia de bromură de litiu se foloseşte ca agent de deshidratare în instalaţiile industriale pentru producerea frigului. În acest scop soluţia se condiţionează cu 1% alcool izooctilic şi azotat de litiu (ca inhibitor de coroziune).

Limitele recomandate de azot de litiu fiind de 350...550 ppm se impune deci o separare a acestuia şi un control riguros în soluţie.

Se prezintă posibilităţile de îndepărtare a urmelor de azotat prin trecerea soluţiilor ce conţin acest ion pe o răşină schimbătoare de ioni cationică forma argint.

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Co(II), Ni(II), Cd(II) AND Zn(II) CONCENTRATION WITH A STRAIN OF *SACCHAROMYCES CEREVISIAE*

BY

VIORICA DULMAN and CONSTANŢA BURCOVEANU

1. Introduction

Taking into consideration the results obtained in concentration and separations of metallic ions in dilute solutions with various yeasts species [1], [2], testings have been carried out on a *Saccharomyces cerevisiae* strain for the concentration of Cu(II), Ni(II), Cd(II) and Zn(II) ions. The aim of these testings has been to explore this yeast characteristics of accumulation heavy metallic ions so that it might be used as a microbiological collector to remove some Cu(II), Ni(II), Cd(II) and Zn(II) toxic ions from waste waters (for instance, waters comming from electroplating processes).

2. Experimental

1.2. Materials and Method

The experiment was carried out on a *Saccharomyces cerevisiae* strain isolated, maintained and standardized in a manner similar with the one described in previous papers [1], [2]. As it is a rather laborious task to get a suspension of a pure strain of *Saccharomyces cerevisiae* in laboratory conditions (it requires a previous growing on adequate media), the experiment was carried out on only one amount of suspension corresponding to 0.149 g dry mass for 50 ml solution (m). For an inocul we used a certain volume of standardized suspension that was introduced in phosphate buffer (50 ml), pH = 6.3, 2% glucose was added as energetic support, standard solutions of various concentrations in Cu(II), Ni(II), Cd(II), Zn(II).

The standard solutions were prepared from nitrates for Ni(II) and Cu(II), phosphate for Cd(II) and chloride for Zn(II).

The samples were kept under static conditions, at room temperature ($20° \pm 2°C$). The supernatant was maintained clear until the experiments were over $\sim$ 5 days. At certain time intervals 2 ml samples were taken out to be analysed by atomic absorbtion spectroscopy. The results of the experiment were interpreted along the same lines as in previous papers [1], [2].

3. Results and Discussions

3.1. Cu(II) Concentration

The strain of *Saccharomyces cerevisiae* remove ~99% of Cu(II) in 48 hours (Fig. 1, curve *I*) from solutions containing 1.11 μg/ml and in 72 hours (Fig. 1, curve *II*) 2.18 μg/ml Cu(II). It comes to more concentrated solutions 4.28 μg/ml Cu(II) concentrates 86% in five days (Fig. 1, curve *III*).

3.2. Ni(II) Concentration

Under the above mentioned conditions the strain of *Saccharomyces cerevisiae* accumulates Ni(II) quantitatively from solutions containing 1.27 μg/ml, in five days from solutions with 2.55 μg/ml. With concentrations higher that 6.55 μg/ml Ni(II) is concentrated 95% in five days. Fig. 2 (curves *I*, *II*, *III*) ilustrate Ni(II) accumulation function of its concentration in the medium.

3.3. Cd(II) Concentration

The strain of *Saccharomyces cerevisiae* accumulates 95% Cd(II) at the most in three days from solutions containing 2.73 μg/ml Cd(II), 86% for 1.1 μg/ml Cd(II). From dilute solutions 0.55 μg/ml, in 24 hours 64% is accumulated and this amount keeps constant over the 1...3 days interval after which Cd(II) is released in the medium reaching 36% in four days (Fig. 3, curve *I*). The same Cd(II) release in the medium is noticed after three days in the previous instances (Fig. 3, curves *II*, *III*).

3.4. Zn(II) Concentration

~99% Zn(II) can be concentrated from solutions containing 0.5 μg/ml in three days, the accumulation rate being the same after four days (Fig. 4, curve *I*). From solutions containing 1 μg/ml and 2.5 μg/ml Zn(II) is accumulated 70% and 60% respectively, in three days after which Zn(II) is slowly released into the medium (Fig. 4, curves *II*, *III*).

3.5. Cu(II), Ni(II), Cd(II), Zn(II) Accumulation with a Strain of *Saccharomyces cerevisiae* when Glucose is Absent

The accumulation and intracellular transport of some bivalent metallic ions with yeasts is an issue studied by several authors in order to clear up the accumulation mechanism as well as to draw certain conclusions concerning the part that some elements play in respiratory and fermentation processes (glucose) [3] ... [6].

Alongside with the determinations for the study of accumulation of Cu(II), Ni(II), Cd(II), Zn(II) metallic ions by the yeast cells of *Saccharomyces cerevisiae* strain testings have been made on the influence of glucose in this process. The results we got (Fig. 5) show that in this respect, there exist differences function of the metallic ion under study.

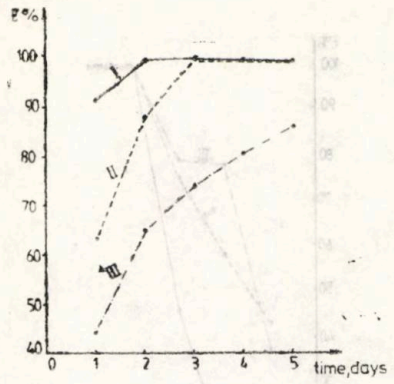

Fig. 1. — Cu(II) concentration with a strain of *Saccharomyces cerevisiae*: *I* — 1.11 μg/ml Cu(II); *II* — 2.18 μg/ml Cu(II); *III* — 4.28 μg/ml Cu(II).

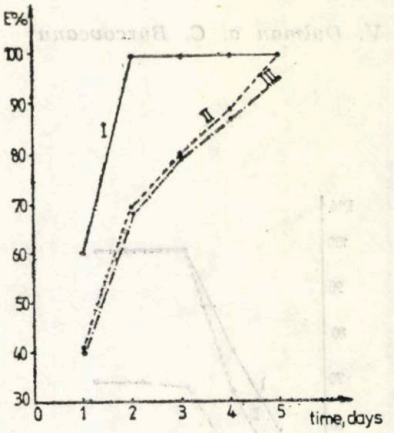

Fig. 2. — Ni(II) concentration with a strain of *Saccharomyces cerevisiae*: *I* — 1.27 μg/ml Ni(II); *II* — 2.55 μg/ml Ni(II); *III* — 6.55 μg/ml Ni(II).

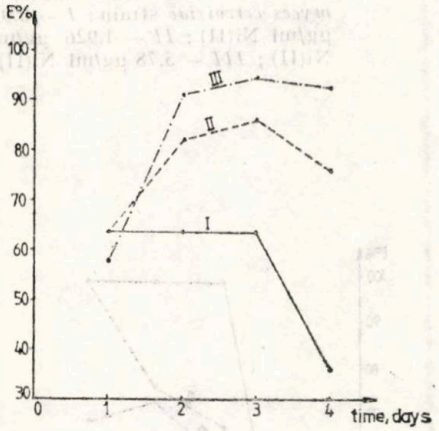

Fig. 3. — Cd(II) concentration with a strain of *Saccharomyces cerevisiae*: *I* — 0.55 μg/ml Cd(II); *II* — 1.1 μg/ml Cd(II); *III* — 2.73 μg/ml Cd(II).

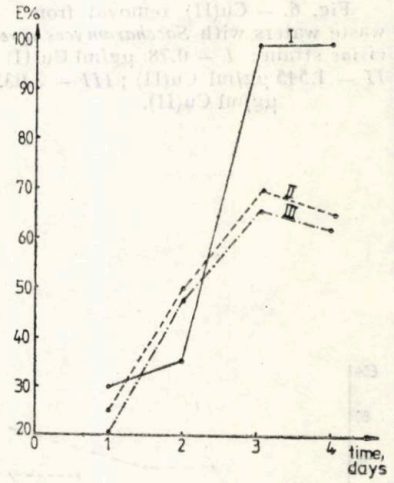

Fig. 4. — Zn(II) concentration with a strain of *Saccharomyces cerevisiae*: *I* — 0.5 μg/ml Zn(II); *II* — 1 μg/ml Zn(II); *III* — 2.5 μg/ml Zn(II).

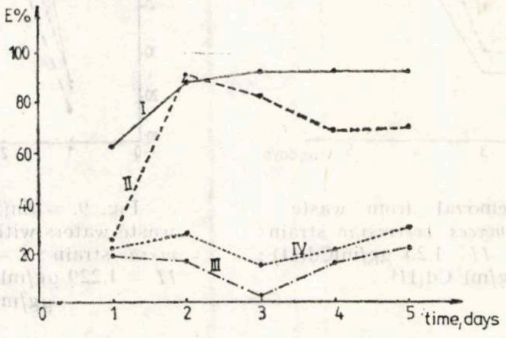

Fig. 5. — The influence of time on Cu(II), Ni(II), Cd(II), Zn(II) concentration with a strain of *Saccharomyces cerevisiae* when glucose is absent: *I* — Cu(II); *II* — Ni(II); *III* — Cd(II); *IV* — Zn(II).

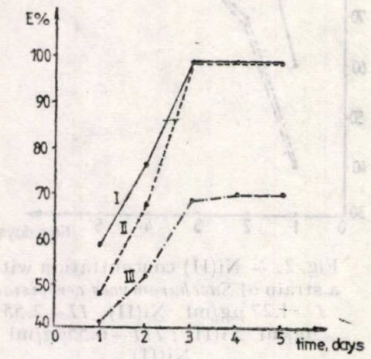

Fig. 6. — Cu(II) removal from waste waters with *Saccharomyces cerevisiae* strain : *I* — 0.78 μg/ml Cu(II) ; *II* — 1.545 μg/ml Cu(II) ; *III* — 3.035 μg/ml Cu(II).

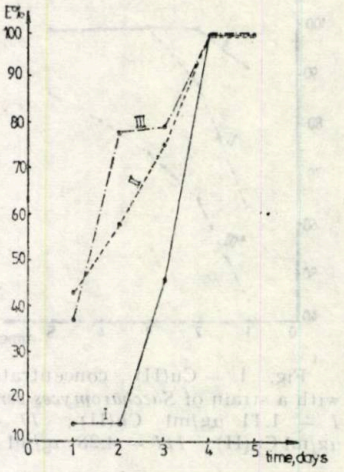

Fig. 7. — Ni(II) removal from waste waters with *Saccharomyces cerevisiae* strain : *I* — 0.93 μg/ml Ni(II) ; *II* — 1.926 μg/ml Ni(II) ; *III* — 3.78 μg/ml Ni(II).

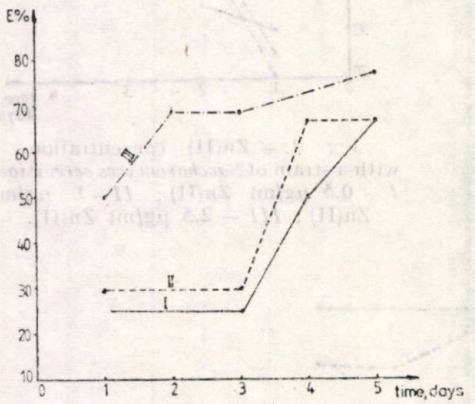

Fig. 8. — Cd(II) removal from waste waters with *Saccharomyces cerevisiae* strain : *I* — 0.75 μg/ml Cd(II) ; *II* — 1.25 μg/ml Cd(II) ; *III* — 2.5 μg/ml Cd(II).

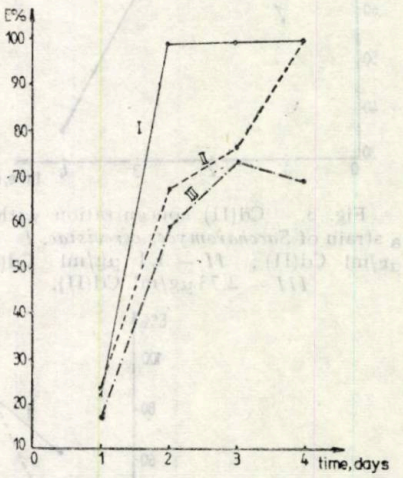

Fig. 9. — Zn(II) removal from waste waters with *Saccharomyces cerevisiae* strain : *I* — 0.637 μg/ml Zn(II) ; *II* — 1.229 μg/ml Zn(II) ; *III* — 2.415 μg/ml Zn(II).

By suspending the yeast cells in phosphate buffer (pH =6.3) with ~1 μg/ml Cu(II) when glucose is absent, significant amounts of Cu(II) are accumulated, a maximum of 90% over an interval of 3 ... 5 days (curve *I*). It is presumable that in this copper accumulation process, glucose is very little implied while adsorbtion, penetration and internal binding of the metallic ion play the main part.

When glucose is absent at ~1.5 μg/ml Ni(II), is accumulated ~24% Ni(II) within the first 24 hours, the accumulation rate goes up to 91% after 48 hours, then it is partially released in the solution (curve *II*). As it was with Cu(II), Ni(II) accumulation is only to a slight extent dependend on the presence of glucose in the medium.

By suspending the yeast mass in phosphate buffer, 1.35 μg/ml Cd(II), when glucose is absent 20% Cd(II) is accumulated within the first 24 hours, when there follows a Cd(II) release in the solution and then an accumulation in time (curve *III*). With Zn(II) ~1.5 μg/ml, the accumulation rate does not go beyond 30% while Zn(II) accumulation takes place as a cyclic adsorbtion and desorbtion process in time. The results we have got prove that Zn(II) and Cd(II) accumulation is to a great extent, dependent on the fermentation process.

There has been noticed a stimulating action of the fermentation process with *Saccharomyces cerevisiae* in the presence of Zn(II) but an inhibition of the respiratory adaptation. It has been proved that Zn(II) is accumulated by *Saccharomyces cerevisiae* by process that are dependend on and independent of energy [3], [4].

3.6. Cu(II), Ni(II), Cd(II), Zn(II) Ions Removal from Waste Waters with *Saccharomyces cerevisiae* Strain

The negative influence of heavy metallic ions from waters upon various forms of life is being presented [7]. The results we got in Cu(II), Ni(II), Zn(II), Cd(II) concentration from standard solutions using *Saccharomyces cerevisiae* yeast led us to the idea of employing it as a „microbiological collector" to remove these metallic ions from industrial residual waters. The experimental results might be affected by the presence in water of some substances that inhibit or accelerate certain microbiological processes.

The *Saccharomyces cerevisiae* strain (m =0.149 g) can remove quantitatively : Cu(II) present in solutions with 0.787 ... 1.54 μg/ml in three days (Fig. 6) ; Ni(II), 0.93 ... 3,78 μg/ml in four days (Fig. 7) ; Zn(II) in two days for concentrations up to 0.637 μg/ml and in four days for concentrations of 1.229 μg/ml (Fig. 9) ; Cd(II) is removed at the most from 67% to 77 % from solutions containing from 0.75 μg/ml to 2.5 μg/ml in five days (Fig. 8).

From a residual water containing ⩽0.6 μg/ml Cu(II), ⩽0.8 μg/ml Ni(II), ⩽0.8 μg/ml Zn(II), ⩽0.3 μg/ml (Cd(II) with the same technique employed for individual ions, with a yeast mass of *Saccharomyces cerevisiae* m =0.149 g, a removal of ~99% Cu(II) was achieved in one day ; Ni (II) in three days : Zn(II) and Cd(II) in two days. A release of the Cd(II) accumulated in the medium has been noticed after a 48 hours interval.

4. Conclusions

1. From the data presented results that ions of Cu(II), Ni(II), Zn(II) and Cd(II) at most 95% can be quantitatively concentrated with *Saccharomyces cerevisiae* strain as a microbiological collector under the given conditions.

2. The accumulation process mediated by *Saccharomyces cerevisiae* strain is influenced by the presence of glucose in the medium, with Zn(II) and Cd(II) and to a small degree for Cu(II) and Ni(II). Thus we could presume an active transfer of Zn(II) and Cd(II) ions within the cells and for Cu(II) and Ni(II) a sorbtion at the cell surface. *Saccharomyces cerevisiae* strain behaves as a selective ion exchanger, the change transfer being favoured by the cell structure of the microorganism, by the nature of the ion used, the medium composition. Intracellular enzymes, — SH anionic groups participate in the metallic ion concentration this way.

3. The results we have got with the removal of the above mentioned ions from residual waters have proved that the major water components can be removed by classical methods but that microbiological collectors turn profitable when traces of these elements are detected, traces that have a noxious effect on some forms of life.

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CONCENTRAREA Cu(II), Ni(II). Cd(II) şi Zn(II) CU O TULPINĂ DE *SACCHAROMYCES CEREVISIAE*

(Rezumat)

O tulpină de *Saccharomyces cerevisiae* a fost utilizată în calitate de „colector microbiologic" pentru concentrarea Cu(II), Ni(II), Cd(II) şi Zn(II) din soluţii diluate. În acest scop s-au studiat condiţiile de pH, timp, concentraţia elementelor şi influenţa glucozei asupra acestui proces. S-au obţinut rezultate satisfăcătoare la îndepărtarea urmelor ionilor menţionaţi, cu tulpina de *Saccharomyces cerevisiae*, din ape reziduale.

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D.C. 546.98 ; 546.57 ; 546.49 ; 661.8...713

COMPLEX COMBINATIONS OF TRANSITION METALS WITH THE MERCAPTOPROPIONIC ACID

BY

OLGA VICOL, N. FOCA, L. CRIŞAN and A. CIUNGRADI

1. Introduction

SH
|

The mercaptopropionic acid, CH_2-CH_2-COOH, acts as a bidented ligand by means of its two functional groups : — COOH and —S—H [1].

As both — COOH and —SH groups can dissociate, when interpreting the results the ionization constants of the propionic acid hydrogen sulphide and β-mercaptopropionic acid must be taken into account. The values of these constants, as given in the literature are :

CH_3-CH_2-COOH	$K_a = 1.6 \times 10^{-5}$;
H_2S	$K_{a1} = 3.3 \times 10^{-7}$, $K_{a2} = 2 \times 10^{-15}$;
$HS-CH_2-CH_2-COOH$	$K_{a1} = 3.6 \times 10^{-4}$.

It results from the above data that the biggest value of the ionization constant, K_a, is found in the case of the propionic acid. In both dissociation steps H_2S shows small values of K_a.

These facts lead to the conclusion that the —SH group in the mercaptopropionic acid acts as a donor in the interaction with Ag(I), Hg(II) and Pd(II) ions [2], [3].

2. Experimental Part

This work shows a series of data concerning the preparation, chemical analysis and IR spectra of some complex combinations of mercaptopropionic acid with Pd(II), Hg(II) and Ag(I) ions.

Solutions of $PdCl_2$ in HCl, $HgCl_2$ in C_2H_5OH, $AgNO_3$ solutions were used for the preparations of the complexes of these cations with the mercaptopropionic acid.

The solution of ligand (L) mercaptopropionic acid, $HS-CH_2-CH_2-COOH$, must be heshly prepared because after a bigger time interval some chemical processes take place. Thus we observed that after 6 ... 7 days the solution deposits a white precipitate as the results of an oxidation process which can be expressed as :

$$\begin{array}{l} CH_2-SH \\ | \\ CH_2 \\ | \\ COOH \end{array} + \frac{1}{2}O_2 + \begin{array}{l} HS-CH_2 \\ | \\ CH_2 \\ | \\ HOOC \end{array} \longrightarrow \begin{array}{l} CH_2-S-S-CH_2 \\ | \quad\quad | \\ CH_2 \quad CH_2 \\ | \quad\quad | \\ COOH \quad COOH \end{array} + H_2O.$$

In this process a white precipitate results, with a reduced solubility, which deposits itself in time. The chemical analysis and IR spectra of this

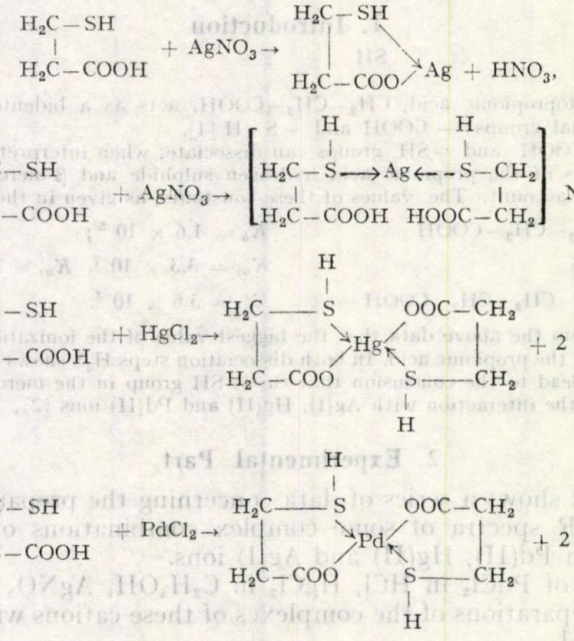
product confirm the above proposed structure. The concentration of the solutions we worked with ranged between 1×10^{-1} moles l^{-1} for the ligand and 1×10^{-1} ... 4×10^{-2} moles l^{-1} for $PdCl_2$, $HgCl_2$ and $AgNO_3$.

3. Results and Discussion

The reaction of 3-mercaptopropionic acid with Pd(II), Hg(II) and Ag(I) is a test one. The mixing of the reactants results in compounds with a reduced solubility, precipitating in the solution.

Thus, for the concentrations we worked with, the appearance of the precipitate takes place after 10 ... 15 min.

The forming reactions of the compounds obtained by us, as a consequence of the reactions between Ag(I), Hg(II), Pd(II) and the β-mercaptopropionic acid can be formulated as follows :



The complex compounds resulted from these reaction are separated by filtering from the solution and dried for a few hours in an oven at 105° ... 110°C.

The resulted compounds were analysed both chemically and in IR. The IR spectra of the new complexes were compared with that of the free ligand. The spectra have been recorded in KBr (Merck).

The chemical analysis of these compounds lead us to the conclusion that they have a combining rate M : L ranging from 1 to 3 as a results of the interactions we represented above.

Thus, for Ag(I) ion two compounds result : AgL and AgL_2 while for Hg(II) and Pd(II) ions with a molar ratio 1 : 2 complexes such as HgL_2 and PdL_2 appear.

Table 2

Absorbtion Band Characteristics of the Complexes of Mercaptopropionic Acid with Ag(I), Hg(II), Pd(II) ions, [cm^{-1}]

Ligand CH_2-CH_2-COOH | SH	AgL	AgL_2	HgL_2	PdL_2	Attribution of bands
645 (medium wide band)	655 (shoulder)	635 (small band) 665 (shoulder)	647 (intense band)	620 690 (shoulder)	$\nu_{C-S\ sym.}$
1 690 (intense band)	1 650 (medium wide band)	1 690 (intense band)	1 680 (intense band)	1 670 (intense band)	$\nu_{COO^-\ antisym.}$
1 390 (intense band)	1 340 (medium wide band)	1 400 (great band)	1 420 (great band)	1 370 (intense band)	$\nu_{COO^-\ sym.}$
3 000 (intense great band)	3 020 (shoulder) 3 220 (great band)	3 010 3 090 (shoulder) 3 220 (great band)	3 040 (great band) 3 300 3 580 (shoulder)	3 040 (great band) 3 300 3 580 (shoulder)	$\nu_{OH^-\ sym.}$
2 550 (shoulder)	—	2 570 (shoulder) 2 630 (small band)	2 580 (shoulder)	2 580 (shoulder)	$\nu_{SH\ sym.}$
2 640 (small band)	—		2 640 (small	—	$\nu_{SCH_2\ antisym.}$
1 390 (small band)	—	1 400 (great band)	1 420 (intense)		$\nu_{SCH_2\ sym.}$

The data obtained from the chemical analysis of the prepared complex combinations are given in Table 1 [4].

Table 1

Chemical Analysis of some Complex Combinations of 3-Mercaptopropionic Acid with Ag(I), Hg(II) and Pd(II)

Nr.	Compound	Colour	M, [%]		C, [%]		H, [%]	
			calc.	found	calc.	found	calc.	found
1	AgL	Yellow	50.4	49.3	16.95	16.00	2.35	2.52
2	AgL_2	Yellow	26.0	25.3	33.90	34.65	4.70	4.48
3	HgL_2	White	48.6	47.8	17.50	18.28	2.43	2.62
4	PdL_2	Orange	33.4	32.29	22.73	23.50	3.15	3.53

The IR Spectra of the mercaptopropionic acid and of the complexes we prepared were recorded by the method with KBr using a Perkin Elmer Spectrophotometer.

The characteristics of the IR absorbtion bands of the free ligand and of complexes are given in Table 2.

From the comparative study of the IR absorbtion bands for the free ligand and complexes it results that the band 3 000 ... 3 600 cm^{-1} is strongly modified.

The characteristic frecquencies of the $-SH$, $-C-S$, $-S-CH_2$ groups are also affected, as showen in Table 2.

The comparative study of IR spectra of the ligand and complex combinations we prepared suggests that the $-COO^-$ group coordinates by ionic bond while the $-SH$ group by coordinative bond to the metallic ions [5].

4. Conclusions

In conclusion the results of the chemical analysis and of the IR spectra provide the formulated structures for the complex compounds of 3-mercaptopropionic and Ag(I), Hg(II) and Pd(II) ions we prepared [6].

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COMPLECȘI AI Pd(II), Ag(I) ȘI Hg(II) CU ACIDUL β-MERCAPTOPROPIONIC

(Rezumat)

Acidul β-mercaptopropionic reacționează cu o serie de cationi ai metalelor tranziționale formînd combinații complexe.

Astfel, sărurile de Pd(II), Ag(I) și Hg(II) reacționează cu acest ligand

$$CH_2-CH_2-COOH$$
$$|$$
$$SH$$

formînd combinații greu solubile, ușor de separat din mediul de reacție.

Complecșii obținuți au fost analizați chimic prin spectrofotometrie în IR cît și prin analiză termică diferențială.

Datele obținute prin analiza chimică arată că în cazul Ag(I) se formează doi compuși chimici, AgL și AgL_2, în timp ce în cazul ionilor de Pd(II) și Hg(II) se formează numai complecși PdL_2 și HgL_2.

Studiul spectrelor în IR ale complecșilor comparativ cu cele ale ligandului liber, dovedește coordinarea acestui ligand prin grupele —SH și —COOH.

Combinațiile obținute sînt insolubile în apă și în majoritatea solvenților organici.

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D.C. 54-92 ; 66.063.8

STUDY ON THE COMPATIBILITY OF SOME POLYMER MIXTURES

II. POLYPROPILENE—COPOLYESTER (PET + PG 5%) FROM COMMON SOLVENT

BY

ELENA MIHAI, MARIANA LUCHIAN and M. FURNICĂ

1. Introduction

Data on compatibility of some polypropilene (PP)—copolyester (CPE) mixtures obtained from melts were reported in a previous paper [1]. The results evidenced the fact that among the investigated mixtures that of the composition 85% PP — 15% CPE exhibited the highest compatibility, achieved by a highest interaction and a better interpenetration of phases, homogeneous mixtures being thus obtained [2], [3].

The present paper is aimed to study the mixtures obtained from the same components by precipitating from common solvent in order to point out the fact that the procedure by which the mixture is obtained (melt or a common solvent) affects the compatibility degree.

2, Experimental

The following mixtures were studied: 95% PP +5% CPE —(*A*) ; 90% PP +10% CPE —(*B*) ; 85% PP +15% CPE —(*C*) ; 80% PP +20% CPE —(*D*) ; 70% PP +30% CPE —(*E*) and 50% PP +50% CPE —(*F*).

For each mixture 50 ml of 2% solution (in volume) were prepared by solving the required amount of PP in 25 ml decaline and of CPE in phenol-tetrachlorethane mixture under stirring and heating at 130°...140°C. After the complete dissolution of both polymers the two warm solutions were mixed by dropping the CPE solution into PP one, under stirring.

For precipitating absolute methanol was used ; the obtained precipitate was dried at 60°...70°C, for two hours in an oven.

The samples were investigated by using optical microscopy, thermogravimetrical analysis and IR spectroscopy.

2.1. Optical Microscopy

The film samples were studied by means of an IOR microscope in phase contrast with 10 ocular and PL-40 objective. The images have been photographed at an exposure time of 12 sec., the overall amplification being of 600 times.

The careful examination of the photographs given in Fig. 1 indicated the mixture (*C*) to be the most homogeneous, in agreement with data obtained by analysing the mixtures obtained from melts.

A more advanced homogenization is noticed in case of samples obtained from melts.

2.2. Thermogravimetrical Study

The samples obtained by precipitation from a common solvent were submitted to thermal degradation under dynamic temperature conditions on a MOM-Budapest derivatograph under the same conditions as in case of samples obtained from melts. From the obtained curves the values of apparent energy of activation were calculated using the differential method (graphical plotting $dc/d\tau$ vs. C, where C denotes the conversion at a given reaction time) [4].

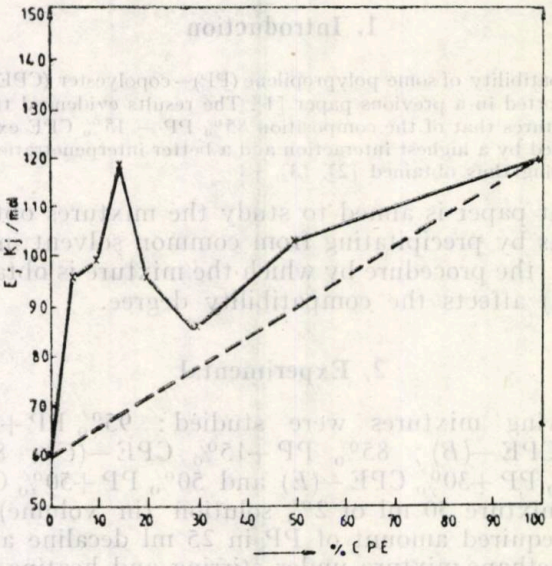


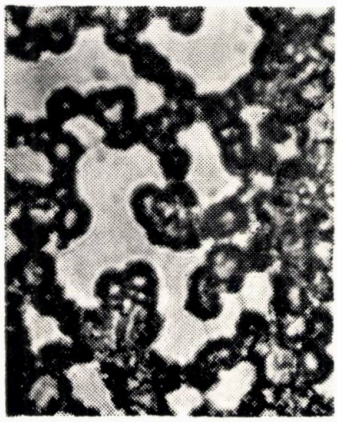
Fig. 2. — Variation of apparent energy of activation against the mixture composition.

The variation of apparent energy of activation against the mixture composition is depicted in Fig. 2.

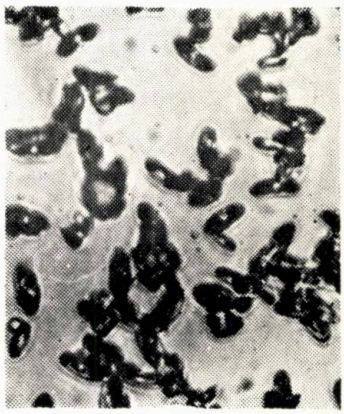
The presence of a maximum is noticed, which indicates the mixture (*C*) to have a higher pseudocompatibility similar to that of mixtures of the same components, obtained from melt. The existence of a low packing density of chain is probably implied.

2.3. IR Spectroscopical Study

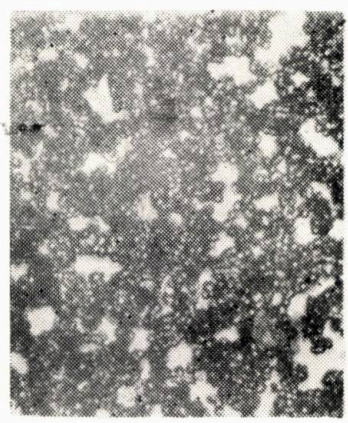
To find the eventual interactions in IR spectra the variation of characteristical bands were followed.



a



b



c

Fig. 1. — Photographs obtained for PP (*a*), CPE (*b*) and the mixture (*C*) (*c*) by optical microscopy.

To remove a possible influence of the film thickness the relative optical densities were calculated.

For the copolymer (PET+PG 5%) the bands at 1 710 cm^{-1} were considered (band characteristic of $-\overset{\overset{O}{\|}}{C}-$) and at 1 765 cm^{-1} while for polypropilene those at 1 365 cm^{-1} and 1 440 cm^{-1} (asymmetrical and symmetrical bands for $-CH_3$). Within the range of chosen bands the second component does not exhibit particular changes.

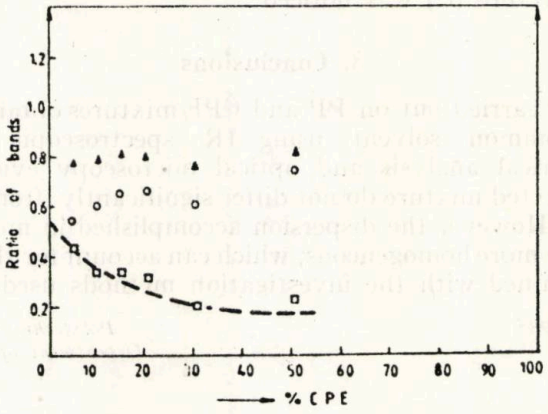


Fig. 3. — Variation of ratio of chosen characteristic bands with mixture composition: ○ — characteristic bands for CPE 765/1 710 cm^{-1}; Δ — characteristic bands for PP 1 440/1 365 cm^{-1}; □ — characteristic bands for PP isotacticity 975/1 365 cm^{-1}.

The variation of ratio of chosen characteristic bands with mixture composition is depicted in Fig. 3.

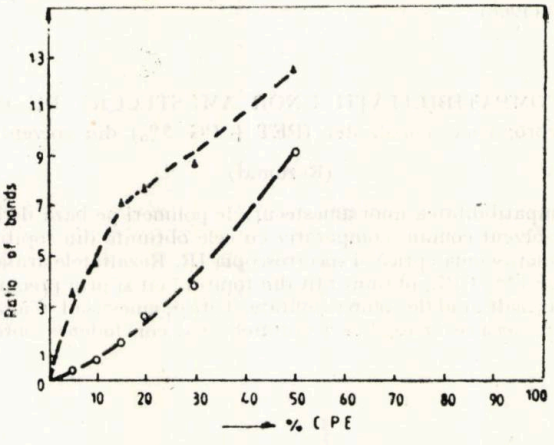


Fig. 4. — Variation of characteristic bands ratio for CPE and PP with mixture composition: ○ — characteristic bands 765/841 cm^{-1}; Δ — characteristic bands 1 710/1 365 cm^{-1}.

No significant changes are to be seen, that means no particular interactions occur in the investigated system. The variation of ratio of 975/1 365 bands, where band at 975 cm^{-1} is the characteristic one for PP isotacticity, indicates a significant influence of ordering due probably to the fact that the mixt package of chains affects the order of isotactic sequences initially present in PP.

If the variation of characteristic band ratio with mixture composition for CPE and PP is followed (Fig. 4) a non linear dependence is found which suggests the existence of certain interactions. In some cases a distinct behaviour of mixture (*C*) was noticed.

3. Conclusions

The study carried out on PP and CPE mixtures obtained by precipitating from common solvent, using IR spectroscopic measurements, thermogravimetrical analysis and optical microscopy evidenced the fact that the investigated mixture do not differ significantly from those obtained from melts [5]. However the dispersion accomplished in melts is more fine, the mixtures are more homogeneous, which can account for the more conclusive results obtained with the investigation methods used.

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STUDIUL COMPATIBILITĂȚII UNOR AMESTECURI DE POLIMERI

II. Polypropilena—copoliester (PET + PG 5%) din solvent comun

(Rezumat)

S-a studiat compatibilitatea unor amestecuri de polimeri pe bază de PP și CPE, obținute prin precipitare din solvent comun, comparativ cu cele obținute din topitură aplicînd metoda termogravimetrică, microscopia optică și spectroscopia IR. Rezultatele arată că amestecul avînd compoziția 85% PP și 15% CPE, obținut atît din topitură cît și prin precipitare din solvent comun, prezintă cel mai înalt grad de compatibilitate. Totuși, amestecul realizat din topitură se prezintă mai omogen, ceea ce ar explica rezultatele mai concludente obținute prin metodele utilizate.

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THE STRUCTURAL–ADSORBTIVE CHARACTERIZATION OF THE MOLECULAR SIEVES SYNTHESIZED IN BASIC, PROTIC, SOLVENT–WATER MEDIUM

BY

EVELINE POPOVICI and M. CRUCEANU

1. Introduction

The use of the organical compounds in the hydrothermal synthesis of the molecular sieves is a new field of the investigation following the acquirement of the zeolitic products with new properties. Now, the studies are developed in two directions : either the use of some raw materials of organical nature, able to provide the basic element required for the carrying out the zeolitic crystalline structure [1], or the use of some raw, inorganic materials, usually natrium or kalium aluminate and silicate, which contact themselves in the presence of some organical compounds [6], [12]. The theoretical justification of the second direction has in view the mechanism of the hydrothermal crystallization of the aluminosilicate gels [4], [5], [7]...[9] which admits that, in a first step, by the depolymerization of the aluminosilicate gel, takes place building up of some basic structural units, which soon after, according to the composition and the nature of the medium may pack up themselves in different ways [12].

In the present paper one investigates the influence of some basic, protic, solvents on the crystallization process and on the properties of the molecular sieves of the NaA type.

2. Experimental

The products synthesis was accomplished using aqueous solutions of natrium silicate and aluminate, concentrated under stirring and have generated the initial composition of : 46.5% moles Na_2O, 27.7% moles Al_2O_3, 25.8% moles SiO_2. The crystallization was realised in 10 hours, at $95° \pm 0.5°C$, in a flask provided with mechanical stirrer, reflux refrigerator and an opening for samples picking [9]. A reference product, C_0, was synthesized in aqueous medium and a series of products C_1 ... C_6 where obtained by simultaneously adding the basic, protic, solvent with the reactants ensuring a constant value of 0.1 of the molar fraction of the used solvent (s. Table 1).

The resulting microcrystalline powder was separated by filtering, washed with not water on the filter till pH = 9 ... 10 and dryied at 110°C.

The characterization of the obtained products was performed by chemical analysis, infrared spectroscopy, thermogravimetry, X-ray diffraction and adsorbtivity.

3. Results and Discussion

The data concerning the used solvents and the chemical composition of the acquired products are listed in Table 1.

Table 1

The Chemical Analysis of the Products

Product	Solvent	The molar composition
C_0	—	1.01 $Na_2O \cdot Al_2O_3 \cdot 1.48$ SiO_2
C_1	$HO-CH_2-CH_2-NH_2$	1.07 $Na_2O \cdot Al_2O_3 \cdot 1.92$ SiO_2
C_2	$(HO-CH_2-CH_2)-NH$	0.99 $Na_2O \cdot Al_2O_3 \cdot 2.18$ SiO_2
C_3	$(HO-CH_2-CH_2)_3-N$	0.97 $Na_2O \cdot Al_2O_3 \cdot 2.20$ SiO_2
C_4	$C_6H_{11}NH_2$	1.02 $Na_2O \cdot Al_2O_3 \cdot 1.98$ SiO_2
C_5	i-$C_3H_7NH_2$	1.00 $Na_2O \cdot Al_2O_3 \cdot 2.08$ SiO_2
C_6	n-$C_3H_7NH_2$	1.26 $Na_2O \cdot Al_2O_3 \cdot 1.97$ SiO_2

The chemical analysis indicates that the products composition (Table 1) is influenced by the nature of the used solvent but this influence has a complex character which may be correlated both with the dielectric constant of the solvent, the geometrical sizes of the solvent molecule and with the chemical peculiarities of the solvent [12]. It is to be noted that the triethanolamine produces the most important changes.

The analysis by X-ray difraction (Table 2) emphasizes the remarkable influence of the triethanolamine on the products structure. Even if the initial chemical composition is characteristic for the preparation of the molecular sieve of the NaA type, obvious structure to the reference product, the presence of triethanolamine in the reaction medium causes deep changes which have as a result the realization of a structure of the NaX type. In the diffraction spectrum of the C_3 product there are all the lines characteristic to the NaX structure, having intensities according to the A.S.T.M. file [11]. These profound modifications of the crystallization mechanism reflect the influence of the triethanolamine both on the chemical composition of the basic structural units and on spatial arrangement [12]. One remarks, also, a similar influence of the *iso*-propylamine which has generated a product comprising 10% NaX and 90% NaA. On the considered duration of the synthesis process, the C_1 and C_2 products have a reduced degree of crystallization and in the case of the others products is preserved the structure of the NaA type.

The reaction conditions justify the question if the action of the investigated substances is limited only to that of solvent existent in the reaction and crystallization medium, or if these participate in the lattice formation, or are found adsorbed on the zeolitic surface.

The IR spectral analysis indicates that the crystalline structure of the products is realized by the same bonds, Si—O and Al—O, as well as in the reference product case, and the bonds between the anionic carcass

Table 2

The Analysis by X-Ray Diffraction

Product C_0		Product C_3		Product C_4		Product C_5		Product C_6	
dÅ	I/I_0	dÅ	I/I_0	dÅ	I/I_0	dÅ	I/I_0	dÅ	I/I_0
12.199	100	14.470	100	12.341	95	14.341	40	12.271	95
8.631	70	8.841	30	8.702	80	12.203	100	8.668	85
7.041	40	7.496	25	7.088	45	8.668	85	7.088	50
5.459	30	6.323	10	6.395	10	7.471	10	6.341	19
4.312	10	5.713	35	5.495	35	7.088	45	5.495	30
4.073	40	4.819	10	4.343	10	6.364	15	4.351	15
3.693	60	4.437	20	4.089	10	5.482	35	4.097	60
3.395	20	3.946	10	3.706	95	4.089	60	3.706	100
3.275	60	3.819	10	3.405	25	3.706	100	3.405	25
2.972	70	3.675	20	3.282	80	3.399	35	3.277	85
2.887	10	3.339	55	2.980	100	3.277	90	2.977	95
2.737	15	3.046	15	2.892	20	2.977	100	2.992	15
2.672	5	2.939	20	2.744	25	2.892	35	2.744	25
2.610	40	2.883	55	2.681	10	2.744	30	2.681	10
2.499	10	2.795	25	2.620	65	2.673	20	2.620	65
2.449	10	2.665	25	2.507	10	2.620	70	2.507	10
2.356	5	2.620	10	2.454	10	2.507	10	2.454	5
2.241	5	2.403	10	2.367	5	2.169	15	2.367	5
2.163	10	2.210	10	2.241	5	2 135	10	2.241	5
		2 190	10	2.179	15	2.048	15	2.169	15
		2.121	15						

and the used solvents are not present. Also, is not ascertained the presence of the adsorbed solvents on the surface and unremoved by washing.

In Table 3 one find the results of the thermogravimetric analysis of the obtained products, beforehand prepared by the removal of the water adsorbed on the surface.

Table 3

The Thermogravimetric Analysis

Product	The endothermal effect		Loss %	The exothermal effects		
	Maximum I	Maximum II		Start	Maximum I	Maximum II
C_0	220	440	22.22	840	870	940
C_1	157	350	14.50	—	910*)	960*)
C_2	150	350	13.00	—	—	—
C_3	220	440	22.21	840	870	970
C_4	150...290	440	14.22	850	865	930
C_5	220	440	23.01	840	860	940
C_6	220	440	21.04	820	860	925

*) small intensity.

The reduced intensity of the exothermal effects found in the thermogravimetric curve of the C_1 and C_2 products, as well as the water elimination with maximum rate, at the 150°... 190°C temperature, are facts attesting an unsatisfactory crystallization and support the results of the X-ray diffraction analysis.

In the case of the others products the total loss of water, which represents actually the crystallization water constant, takes values of 20... 23% and are comparable with the data from the literature for the molecular sieves [10].

The thermal stability of the cristalline products, evaluated according to the starting temperature of the exothermal effects, is not modified against the reference, offering the possibility of their use in different adsorption processes taking place at lower temperatures as the thermal degradation temperature.

The determination of the adsorption isotherms of the nitrogen, at —195°C, indicated, for the reference product, an adsorption capacity of 0.70 mmol/g, at equilibrium, while the C_3 product has an adsorption capacity of 4.5 mmol/g, at equilibrium. These differences are dependent of the

Table 4

The Adsorption Properties

Product	S m²/g	The static adsorption capacity, [%]	
		water	benzene
C_0	701.02	24.21	1.11
C_1	383.21	16.50	0.86
C_2	301.92	18.17	1.03
C_3	807.12	27.52	21.41
C_4	688.14	24.18	1.23
C_5	705.14	24.20	3.38
C_6	700.92	22.40	1.20

crystallo-chemical structure and of the extent of specific surface. Also, the changes which have taked place in the morphology of the structure of the products synthesized in the presence of the basic, protic, solvents are reflected in theirs selectivity in the adsorbtion processes (Table 4).

4. Conclusions

In the present paper was investigated the influence of some basic, protic, solvents in the crystallization medium of the molecular sieve NaA on the structural — adsorptive properties of the synthesized products. One notes, particularly, the influence of the triethanolamine on the structural morphology, a fact which has deep implications on the adsorption properties, as well as on the selectivity.

The use of the solvents during the crystallization period of the molecular sieves constitutes a way of convenient influence of chemical composition, of the structure, of the adsorbtive properties and of the uses of the molecular sieves.

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CARACTERIZAREA STRUCTURAL—ADSORBTIVĂ A SITELOR MOLECULARE SINTETIZATE ÎN MEDIU APĂ—SOLVENT PROTIC BAZIC

(Rezumat)

Se studiază influența unor solvenți protici bazici, prezenți în mediul de cristalizare a sitei moleculare NaA, asupra proprietăților structural—adsorbtive a produselor sintetizate. Se remarcă, în special, influența trietanolaminei asupra morfologiei structurale, fapt care are adînci implicații asupra proprietăților de sorbție și asupra selectivității.

Folosirea solvenților în mediul de sinteză a sitelor moleculare constituie un mod de influențare convenabilă a compoziției chimice a structurii, a proprietăților adsorbtive și a utilizărilor sitelor moleculare.

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PRÉPARATION DE L'ACIDE LACTOBIONIQUE

PAR

SAVEL IFRIM, CRISTINA LUCHIAN et M. CRUCEANU

1. Introduction

On obtient l'acide lactobionique par oxydation modérée du disaccharide lactobiose. Ce produit présente une importance particulière pour la préparation du lactobionate de l'érythromycine, un composé injectable intraveineux de l'étythromycine [1]. En Roumanie on prépare le lactobionate de l'érythomycine à l'Usine d'Antibiotiques de Jassy [2], en utilisant de l'acide lactobionique importé.

On indique dans la littérature plus ancienne [3]...[5] que l'acide lactobionique peut être préparé par l'oxydation du lactobiose dissous dans l'eau, en présence du brome, le processus d'oxydation étant prolongé plusieurs jours. Dans ces conditions on obtient de l'acide lactobionique, qui est ensuite, séparé comme sel de calcium.

Compte tenu de l'importance pratique de ce produit, dans ce qui suit on montre la possibilité de préparer l'acide lactobionique comme solution aqueuse, par oxydation électrochimique du lactobiose. En principe cette méthode consiste dans l'oxydation du lactobiose en présence d'une petite quantité de bromure de potassium et de carbonate de calcium ; le carbonate de calcium se trouve comme suspension dans le milieu de réaction.

L'acide lactobionique résulté dans le processus d'oxydation réagit avec la carbonate de calcium, qui est consommé graduellement et il apparaît du lactobionate de calcium. Après la purification, la solution de lactobionate de calcium est passée sur un changeur d'ions en forme hydrogène [6] et il résulte une solution pure d'acide lactobionique.

2. Partie théorique

Le lactobiose est formé d'une molécule de glucose et d'une autre de galactose ; le groupe aldéhydique en s'oxydant au groupe carboxylique il est lié au reste de glucose. Si on hydrolyse l'acide lactobionique il apparaît du galactose et de l'acide gluconique [7].

Le mécanisme d'oxydation des aldéhydes aux acides carboxyliques n'est pas simple. Dans le cas des aldéhydes solubles dans l'eau on accepte que ces composés s'oxydent sous forme d'hydrates, l'agent oxydant étant un accepteur d'hydrogène [8]. Pendant le processus d'oxydation électrochimique du lactobiose dans le milieu aqueux et en présence du bromure de potassium, on peut admettre que l'agent oxydant (accepteur d'hydrogène) c'est l'oxygène actif résultant comme conséquence de la décomposition

de l'eau par le brome. La formation du brome est confirmée par l'odeur caractéristique apparaissant tout de suite après le début de la réaction. Sans doute le brome apparaît à l'anode par l'oxydation de l'anion de brome selon le schéma :

$$2\,Br^- \rightarrow Br_2 + 2e^-$$

et encore

$$Br_2 + H_2O \rightarrow HBrO + HBr$$

$$HBrO \rightarrow O + HBr,$$

$$R-CH(OH)(OH) + O \rightarrow R-C(OH)(OH)(OH)$$

$$R-C(OH)(OH)(OH) \rightarrow R-COOH + H_2O$$

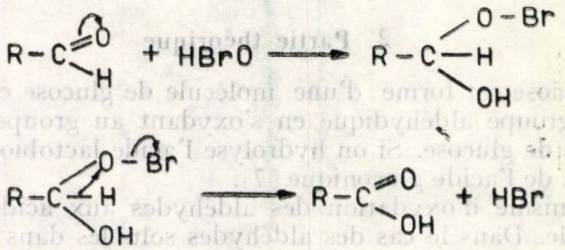
ci R représente le reste de lactobiose ayant la formule moléculaire $C_{11}H_{21}O_{10}-$. Si l'on effectue la somme des ces étapes du processus d'oxydation, il en résulte la suivante réaction générale :

$$2\,Br^- + R-CH(OH)(OH) \rightarrow R-COOH + 2\,HBr + 2e^-$$

Ce mécanisme de réaction est justifié par la propriété oxydante de l'acide hypobromeux, qui se décompose par chauffage, à savoir :

$$HBrO \rightarrow HBr + O.$$

On peut admettre que le processus d'oxydation du groupe aldéhydique se déroule selon un mécanisme d'addition de l'acide hypobromeux à la double liaison carbonyle :



On peut considérer une réaction globale de l'oxydation, quand il apparaît du lactobionate de calcium, selon le schéma :

$$2\,C_{11}H_{21}O_{10}-CHO + O_2 + CaCO_3 \xrightarrow{KBr} (C_{11}H_{21}O_{10}-COO)_2Ca + CO_2 + H_2O$$

3. Partie expérimentale

Dans un récipient ayant une capacité de deux litres, muni de deux électrodes identiques de graphite, on introduit 1 000 ml de l'eau et sous agitation 200 g lactobiose pur, 60 g carbonate de calcium pharmaceutique et 30 g bromure de potassium p.a.

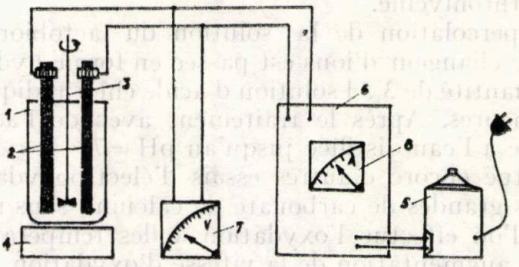


Fig. 1

Le schéma de l'installation de travail est présenté dans la Fig. 1 où : *1*—récipient; *2*—électrodes; *3*—agitateur mécanique; *4*—chauffage électrique; *5*—autotransformateur ; *6*—redresseur ; *7*—voltmètre ; *8*—ampermètre.

On augmente la température du mélange de substances, sous agitation continue, jusqu'à 60°C et on établit une densité de courant électrique de 2,3 A dm^{-2}. On conduit l'électrooxydation pendant 45 ... 50 h en effectuant le contrôle du contenu en lactobiose périodiquement. Le contrôle de l'oxydation a été réalisé par dosage volumétrique du lactobiose, en utilisant la solution Fehling, ayant à la base la propriété du groupe aldéhydique de réduire le cation Cu^{2+} au Cu^{+}.

Si on constate par analyse que la concentration du lactobiose dans le mélange de réaction diminue sous 1% on arrête le fonctionnement de l'installation. Les résultats des analyses sont présentés dans le Tableau 1.

Tableau 1

Nr. crt.	Durée h	Température °C	Concentration de la lactobiose, [%]
1	0	60	20
2	6	60	17,85
3	14	60	12,60
4	20	60	11,47
5	28	60	8,22
6	33	60	4,92
7	40	60	2,10
8	46	60	0,5

On filtre le contenu du récipient et on ajoute au filtrat 45...50 g charbon actif et toujours sous agitation mécanique, à la température de 50°...55°C,

on effectue une opération d'absorption durant 30 min. On filtre la suspension au vide, sans laver le résidu sur filtre. Le filtrat clair et incolore résulté est passé par une colonne de verre ayant le diamètre de 40 mm et l'hauteur de 500 mm, dans laquelle il y a le changeur d'ions en forme hydrogène, type Amberlit IR-124. La vitesse de percolation a été de 4,2 l/h. À la base de la colonne on collecte la solution pure d'acide lactobionique, ayant un pH =3,5 ... 3,8. Cette solution peut être utilisée pour l'obtention du lactobionate de l'érythromycine.

Après la percolation de la solution du lactobionate de calcium, la colonne avec le changeur d'ions est passée en forme hydrogène par traitement avec une quantité de 3,5 l solution d'acide chlorhydique 10%, opération qui dure deux heures. Après le traitement avec de l'acide clorhydrique, la colonne se lave à l'eau distillée jusqu'au pH =7.

On a effectué encore d'autres essais d'électrooxydation, en utilisant de quantités plus grandes de carbonate de calcium, sans modifier la vitesse d'oxydation. Si l'on effectue l'oxydation à des températures plus élevées on a observé une augmentation de la vitesse d'oxydation, mais il se produit également une évaporation notable de l'eau.

4. Interprétation des résultats

La première observation qui résulte par l'analyse des données expérimentales conduit à la conclusion que l'oxydation du lactobiose, dans les conditions mentionnées ci-dessus, est bien terminée au maximum 50 h.

En utilisant les résultats expérimentaux indiqués dans le Tableau 1 on a construit le graphique présenté dans la Fig. 2, où dans l'ordonné est indiquée la concentration du lactobiose en pourcents et dans l'abscisse le temps de la réaction en heures. Ce graphique met en évidence la diminu-

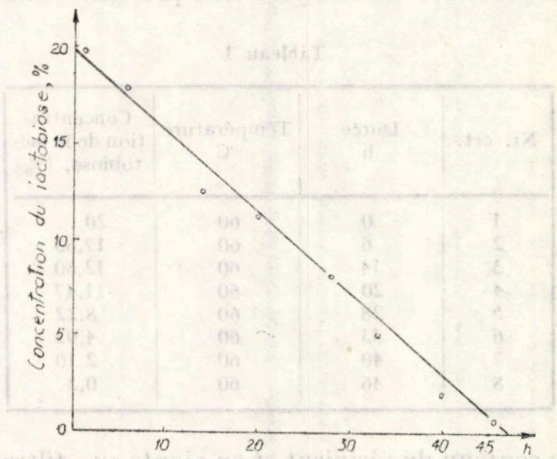


Fig. 2

tion de la concentration de lactobiose en fonction de la durée de réaction. Dans les conditions de ce travail, la réaction d'oxydation électrochimique du lactobiose découle entièrement pendant 47 h.

Compte tenu qu'on a pris pour expérimentation 200 g de lactobiose, par un calcul élémentaire il résulte que la vitesse de l'oxydation est approximativement 4 g/h. On peut interpréter, à l'aide du graphique de la Fig. 2, que la vitesse d'oxydation est assez uniforme, de telle sorte que le processus d'oxydation soit représenté par une droite. Par rapport à cette droite les points du graphique déterminés par voie expérimentale, présentent une petite déviation, qui peut être expliquée par des erreurs expérimentales. On peut également interpréter la déviation des quelques points obtenus par voie expérimentale se trouvant sous la concentration de 8%, par la diminution de la concentration de lactobiose ; on connaît bien que la vitesse de réaction est favorisée par la concentration des réactifs.

5. Conclusions

On étudie l'oxydation du lactobiose à l'acide lactobiomique par voie électrochimique, en résultant les conclusions suivantes :

1. Dans les conditions expérimentales indiquées ci- desous l'oxydation du lactobiose à l'acide lactobionique découle plus rapidement par rapport à la durée connue dans la littérature.
2. On propose les mécanismes chimiques possibles pour le processus d'oxydation du lactobiose à l'acide lactobionique.
3. La présence du bromure de potassium est indispensable au processus d'oxydation et il s'utilise en proportion de maximum 8% par rapport à la quantité de lactobiose ; une proportion plus élevée jaunit la solution.
4. Pour la purification de la solution on utilise du charbon actif type A_3 en proportion de 5% et on travaille à 50° ... 55°C pendant 25 ... 30 min.
5. Pour retenir les ions de calcium la solution a été passée sur un changeur d'ions en forme hydrogène type Amberlit IR-124 ; il en résulte une solution pure de l'acide lactobionique, ayant un pH =3,5 ... 3,8. Cette solution peut être utilisée pour obtenir du lactobionate de l'érythromycine.
6. On utilise le carbonate de calcium en petit excès et il n'influence pas le processus d'oxydation du lactobiose.

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PREPARAREA ACIDULUI LACTOBIONIC

(Rezumat)

Se studiază oxidarea electrochimică a lactozei la acid lactobionic în prezența bromurii de potasiu și a carbonatului de calciu.

Datele obținute arată că în condițiile experimentale precizate în lucrare, oxidarea lactozei la acid lactobionic se petrece mult mai repede decît indică literatura. Prezența bromurii de potasiu este indispensabilă procesului de oxidare. Proporția în acest produs nu trebuie să depășească 8% față de cantitatea de lactoză luată în lucru, spre a nu determina îngălbenirea soluției.

Purificarea soluției de lactobionat de calciu de face cu cărbune activ tip A_3, care se folosește în proporție de maximum 5%, lucrîndu-se la 50°...55°C, timp de 25...30 min. Pentru dedurizarea soluției de lactobionat de calciu se folosește un schimbător de ioni tip Amberlit IR 124, în formă hidrogen. Rezultă o soluție pură de acid lactobionic cu un pH= 3,5...3,8, care se poate folosi la prepararea lactobionatului de eritromicină.

Se propun mecanisme chimice posibile pentru oxidarea lactozei la acid lactobionic.

Carbonatul de calciu nu influențează acest proces de oxidare.

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D.C. 546.22 ; 542.957

ORGANIC SULPHUR COMPOUNDS

XVII [1]. 2-HYDROXYKETONES. XIII [2]. „IASINONES" — NEW MESOIONIC 2-DIALKYLAMINO-1, 3-DITHIOLIUM-*ORTHO*-ORTHOQUINONMONOMETHIDES COMPOUNDS

BY

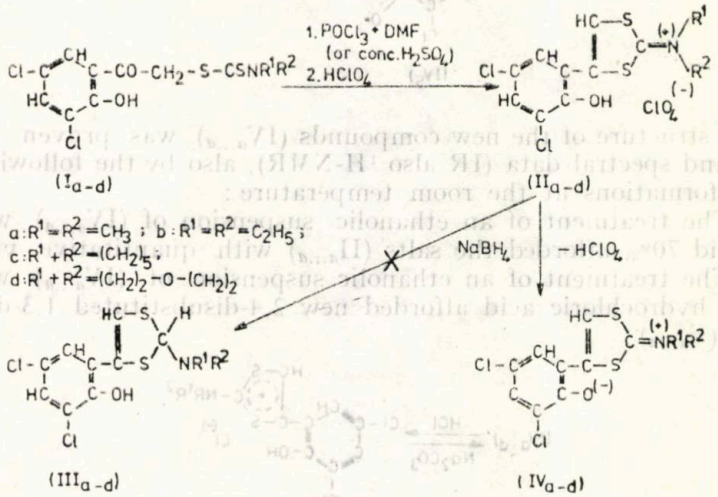
AL. CAȘCAVAL

1. Introduction

Our interest in the synthesis of various organic sulphur compounds [1], also in the chemical reactions of *ortho*-hydroxyketones [2], leads us to a new class of the heterocyclic compounds with mesoionic character. Here we present the synthesis and physical also chemical characterisation of this new five-membered heteroaromatic system.

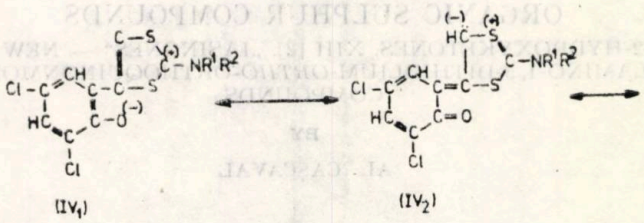
2. Results

β-Ketoalkyl-N,N-dialkyldithiocarbamates ($I_{a...d}$) when treated with Vilsmeier reagent ($POCl_3$ + DMF) in the Harnisch reaction conditions or in a Campaigne reaction (H_2SO_4 conc.) produce 1,3-dithiolium salts characterised as perchlorates ($II_{a...d}$) in high yields :

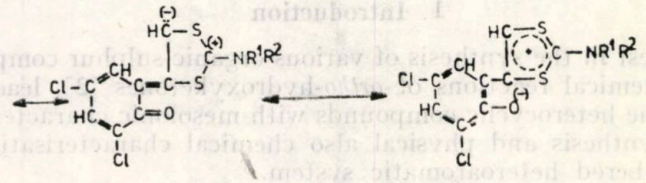


The sodium borohydride reduction [3] products of the 2,4-disubstituted 1,3-dithiolium salts ($II_{a...d}$) are not the expected 2,4-disubstituted

1,3-dithioles ($III_{a...d}$) precursors of the disubstituted tetrathiafulvalene (TTF) — one component of so-called „organic metal" — TTF—TCNQ, the molecular charge—transfer complex with electrically and optically properties like one dimensional metal at the room temperature [4]. The products of this reaction are, in fact, the neutral anhydro-derivatives, well-crystalline compounds with high melting points ($IV_{a...d}$), which can be written as mesoionic [5] compounds :

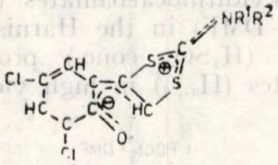


(IV_1) (IV_2)



(IV_3) (IV_4)

or better the mesomeric structure:

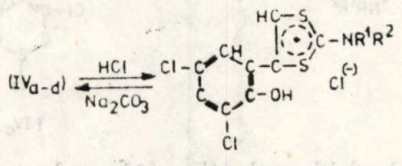


(IV_5)

The structure of the new compounds ($IV_{a...d}$) was proven by microanalysis and spectral data (IR also ^{1}H-NMR), also by the following chemical transformations at the room temperature :

a) The treatment of an ethanolic suspension of ($IV_{a...d}$) with perchloric acid 70% afforded the salts ($II_{a...d}$) with quantitative yields.

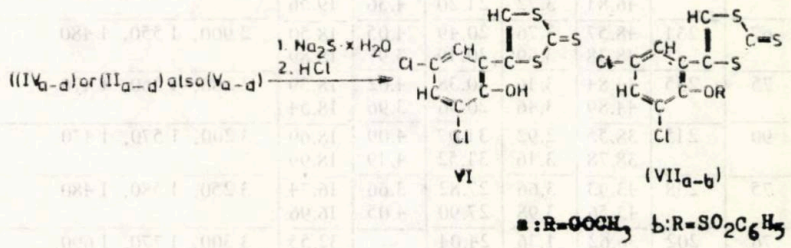
b) The treatment of an ethanolic suspension of ($IV_{a...d}$) with concentrated hydrochloric acid afforded new 2,4-disubstituted 1,3-dithiolium chlorides ($V_{a...d}$) :



(V_{a-d})

An aqueous solution of ($V_{a...d}$) with sodium carbonate afforded again the IASINONES ($IV_{a...d}$) ; so we have obtained in one step the IASINONES without to be obtained perchlorates ($II_{a...d}$) by the treatment of ($I_{a...d}$) with conc. sulphuric acid then the solution was neutralized with sodium carbonate.

c) The treatment of an ethanolic suspension of ($IV_{a...d}$) or ($II_{a...d}$) also ($V_{a...d}$) with an aqueous ethanolic sodium sulphide solution afforded with good yields the trithione (VI) :



4-(3',5'-dichloro-2'-hydroxyphenyl)-2-thioxo-1,3-dithiole (VI) is an important precursor for tetrathiafulvalene also of interest as potential 6-pseudoaromatic system and precursor of the 1,3-dithiolium salts. The phenolic group reacts with acetic anhydride or benzenesulphonyl chloride to give the corresponding esters (VII). The possibility to obtain the new disubstituted tetrathiafulvalene from the products (VI), (VII) are in progress.

These findings lead us to give the name IASINONE for the products (IV) like SYDNONES [6] and MÜNCHNONES [7].

In summary we have reported here the synthesis and some chemical reactions of a new mesoionic class of organic sulphur compounds. The pharmacological screenings of ($V_{a...d}$) are in progress (they are water-soluble compounds).

All experimental data are given in Tables 1 and 2.

3. Experimental Part

IR-spectra were recorded on a Spekord 71 IR spectrometer as KBr-pellets ^{1}H-NMR spectra on a JNM—C—60HL spectrometer in DMSO-d_6 at 20°C.

3.1. General Procedure for the Synthesis of IASINONES ($IV_{a...d}$)

10 mole (I) was disolved by continuous stirring in 20 ml DMF at the room temperature ; 5 ml $POCl_3$ was added by cooling of the reaction mixture in an ice bath (temperature during this addition was maintend at 20°C). A solution of sodium carbonate (50%)was added and the yellow precipitate was filtered and crystallized from DMF (all results are listed in Tables 1 and 2).

3.2. General Procedure for the Synthesis of the Hydrochlorides of IASINONES ($V_{a...d}$)

To a suspension of the IASINONES ($IV_{a...d}$) in acetone is added under vigorous stirring, at the room temperature, concentrated hydrochloric acid (5 ml for 1 mmol) until a clear solution is obtained (15 min). After 5 hours the formed precipitate was filtered off and crystallized from ethanol.

Table 1

Data Concerning the Characterisation (Microanalysis, IR-Spectra) of the Compounds

Compound	Yield %	M.p. °C	C, [%] Calcd. Found	H, [%] Calcd. Found	Cl, [%] Calcd. Found	N, [%] Calcd. Found	S, [%] Calcd. Found	IR(KBr) ν, [cm^{-1}]
(IV_a)	75	293	43.15 42.84	2.94 3.35	23.17 23.30	4.57 4.75	20.92 21.32	2 980, 1 570, 1 470
(IV_b)	85	207	46.72 46.81	3.89 3.72	21.23 21.20	4.19 4.36	19.17 19.56	2 990, 1 530, 1 460
(IV_c)	67	231	48.57 48.38	3.76 3.69	20.49 20.19	4.05 3.97	18.50 18.89	2 900, 1 550, 1 480
(IV_d)	75	235	44.84 44.89	3.16 3.46	20.38 20.56	4.02 3.96	18.39 18.54	2 880, 1 560, 1 470
(V_a)	90	215	38.55 38.78	2.92 3.16	31.07 31.52	4.09 4.19	18.69 18.99	3 200, 1 570, 1 470
(V_c)	75	238	43.93 43.56	3.66 3.98	27.82 27.90	3.66 4.05	16.74 16.96	3 250, 1 580, 1 480
(VI)	76	202	36.62 36.64	1.36 1.48	24.04 23.84	— —	32.55 32.80	3 300, 1 770, 1 690, 1 570, 1 460, 1 060
(VII_a)	52	85...87	39.17 39.07	1.79 1.80	21.02 20.81	— —	28.52 28.22	1 770, 1 720, 1 600, 1 560, 1 450, 1 100
(VII_b)	66	178	41.39 41.53	1.84 1.98	16.30 16.56	— —	29.43 29.87	1 760, 1 670, 1 590, 1 470, 1 200.

Table 2

^{1}H-NMR Spectra of the Prepared Compounds

Compound	Chemical shifts in δ, [ppm] (shape, intensity and assignement of signals)
(IV_a)	3.0 ... 3.5(*s*, 6H, $2CH_3$) ; 7.0 ... 7.3(*m*, 3H).
(IV_b)	1.2 ... 1.5(*t*, 6H, $2CH_3$) ; 3.4 ... 3.8(*q*, 4H, $2CH_2$) ; 7.0 ... 7.2(*m*, 3H).
(IV_c)	2.3 ... 2.8(*m*, 10H, $5CH_2$) ; 7.0 ... 7.3(*m*, 3H).
(VI)	7.45(*m*, 3H) ; 7.80(*s*, 1H)
(VII_a)	3.50(*s*, 3H, CH_3) ; 7.5 ... 7.80(*m*, 3H).
(VII_b)	7.20 ... 7.80(*m*, aromatics protons+ethylenic proton).

3.3. 2-Thioxo-1,3-dithiole (VI) from the IASINONES ($IV_{a...d}$)

To a suspension of the ($IV_{a...d}$) in ethanol was added a sodium sulphide solution (25%) under stirring at the room temperature until a clear red solution was obtained ; the solution was acidified with concentrated hydrochloric acid and the precipitate was filtered off also crystallized from ethanol.

* * *

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COMPUŞI ORGANICI AI SULFULUI

XVII[1]. 2-hidroxicetone. XIII[2]. „IASINONE"—noi compuşi mezoionici de 2-dialchilamino-1,3-ditioliu-*orto*-chinonmonometide

(Rezumat)

Se descrie sinteza şi caracterizarea fizico-chimică a unei noi clase de compuşi mezoinici cu sulf în moleculă. Se propune, în cinstea oraşului IAŞI, denumirea de IASINONE acestei clase de compuşi heterociclici în analogie cu binecunoscutele SIDNONE şi MÜNCHNONE care poartă, de asemenea, denumirea oraşelor corespunzătoare, SIDNEY, respectiv MÜNCHEN.

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D.C. 547.587.51

SYNTHESIS OF SOME MANNICH BASES FROM THE COUMARIN CLASS

BY

TATIANA NICOLAESCU

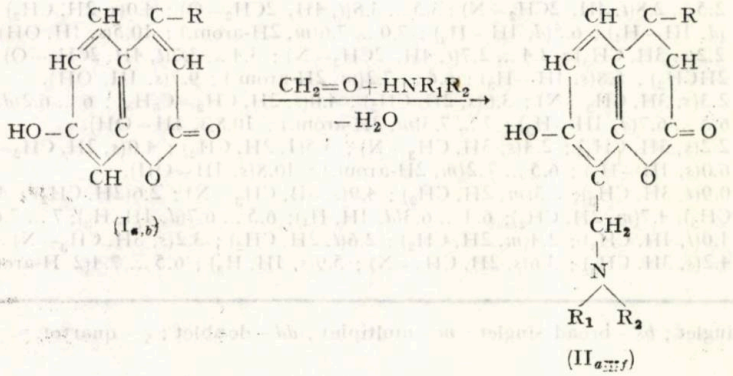
1. Introduction

A series of coumarin derivatives are known possesing antifungicide, rodenticide [1] and antimicrobial properties [2] ... [4] such as 4-phenyl-coumarin, which is a natural compound.

The synthesis of some M a n n i c h bases from 7-hydroxy-coumarin and various primary amines exhibiting biological properties is mentioned in literature [1]. In the present paper the synthesis of six M a n n i c h bases starting from 7-hydroxycoumarin and 7-hydroxy-4-methylcoumarin and secondary amines is reported.

2. Results and Discussion

Six new M a n n i c h bases have been synthesized starting from the coumarines (7-hydroxy-coumarin and 7-hydroxy-4-methylcoumarin [5] — ($I_{a,b}$)), paraformaldehyde and the following amines : morpholine, methyl-*n*-propylamine, methylbenzyl-amine according to the following reaction scheme :



($I_{a,b}$) ($II_{a\ldots f}$)

($I_{a,b}$) : a) R = H ; b) R = CH_3 ;

($II_{a\ldots f}$) : a) R = H ; $R_1 + R_2 = (CH_2)_2 - O - (CH_2)_2$;

b) $R=CH_3$; $R_1+R_2=(CH_2)_2-O-(CH_2))_2$;

c) $R=H$; $R_1=CH_3$; $R_2=CH_2C_6H_5$; d) $R=CH_3$; $R_1=CH_3$; $R_2=CH_2C_6H_5$;

e) $R=H$; $R_1=CH_3$; $R_2=CH_2CH_2CH_3$; f) $R=CH_3$; $R_1=CH_3$; $R_2=CH_2CH_2CH_3$.

The structure of 8-aminomethyl derivatives of 7-hydroxycoumarin and 7-hydroxy-4-methylcoumarin ($II_{a...f}$) is confirmed by elemental analysis (C, H, N) as well as by IR and NMR spectra, according to data in Tables 1 and 2.

Table 1

New Mannich Bases ($II_{a...f}$) Prepared

Compound	m.p. °C	C, [%]		H, [%]		N, [%]		IR cm^{-1}		
		Calc.	Found	Calc.	Found	Calc.	Found			
(II_a)	155	64.30	64.45	5.73	5.67	5.36	5.67	3 180	1 720	1 110
(II_b)	120	65.0	65.28	6.18	5.91	5.09	5.33	3 400	1 700	1 115
(II_c)	95	73.22	73.24	5.76	5.72	4.74	5.07	3 380	1 700	1 100
(II_d)	124	73.78	73.42	6.14	5.68	4.53	4.16	3 400	1 720	1 170
(II_e)	127	68.50	68.53	6.80	6.94	5.66	5.47	3 300	1 700	1 110
(II_f)	120	69.10	69.80	7.27	6.78	5.62	5.30	3 330	1 720	1 115

IR spectra were recorded on a SPEKORD 71 as pellets in KBr.

Table 2

NMR Spectral Data of the New Compounds ($II_{a...f}$)

Compound	Chemical shifts, [ppm] ; (shape), intensity and assignement of signals
(II_a)	2.5 ... 2.8(t, 4H, $2CH_2-N$) ; 3.5 ... 3.8(t, 4H, $2CH_2-O$) ; 4.0(s, 2H, CH_2) ; 5.9 ... 6.1 (d, 1H$-H_4$) ; 6.5(d, 1H$-H_3$) ; 7.0 ... 7.6(m, 2H-arom.) ; 10.5(s, 1H, OH).
(II_b)	2.2(s, 3H, CH_3) ; 2.4 ... 2.7(t, 4H, $2CH_2-N$) ; 3.4 ... 3.7(t, 4H, $2CH_2-O$) ; 3.9(s, $2HCH_2$) ; 5.8(s, 1H$-H_3$) ; 6.6 ... 7.2(m, 2H-arom.) ; 9.7(s, 1H, OH).
(II_c)	2.3(s, 3H, CH_3-N) ; 3.6(s, 2H, CH_2) ; 4.0(s, 2H, $CH_2-C_6H_5$) ; 6 ... 6.2(d, 1H$-H_4$) ; 6.5 ... 6.7(d, 1H$-H_3$) ; 7 ... 7.3(m, 2H-arom.) ; 10.8(s, 1H$-$OH).
(II_d)	2.2(s, 3H, CH_3) ; 2.4(s, 3H, CH_3-N) ; 3.5(1, 2H, CH_2) ; 4.0(s, 2H, $CH_2-C_6H_5$) ; 6.0(s, 1H$-H_3$) ; 6.5 ... 7.2(m, 2H-arom.) ; 10.8(s, 1H$-$OH).
(II_e)	0.9(t, 3H, CH_3); 2.3(m, 2H, CH_2) ; 4.9(s, 3H, CH_3-N) ; 2.6(2H, CH_2) ; 4.0(s, 3H, CH_3); 4.7(m, 2H, CH_2); 6.1 ... 6.3(d, 1H, H_4); 6.5 ... 6.7(d, 1H, H_3); 7 ... 7.6(2H-arom.)
(II_f)	1.0(t, 1H, CH_3) ; 2.4(m, 2H, CH_2) ; 2.6(t, 2H, CH_2) ; 3.2(s, 3H, CH_3-N) ; 4.2(s, 3H, CH_3) ; 3.6(s, 2H, CH_2-N) ; 5.9(s, 1H, H_3) ; 6.5 ... 7.4(2 H-arom.).

s – singlet ; bs – broad singlet ; m – multiplet ; dd – doublet ; q – quartet.

For testing the antimicrobial action of the six Mannich bases the Kyrbi-Bauer procedure of diffusiometric antibiogram was used, the

Mueller-Hinton gel being used as culture medium due to its nutrient value allowing the optimum development of a large variety of germes.

To investigate the inhibitory action of our compounds some strains of pathogene germs were isolated from cultures of pathological products from patients such as : *Coli hemolytic Bacillus, Staphylococcus aureus, Candida albicans, Salmonellae Typhi Murium.* The investigations indicated *Staphylococcus Aureus* to exhibit sensitivity towards the compounds (II_b) and (II_e). The *Coli hemolytic bacillus* and *Salmonellae Typhi Murium* were sensitive only towards product (II_e). Thus the product (II_e) exhibited a more pronounced activity.

3. Experimental

Reaction between 7-hydroxycoumarine and morpholine (compound (II_a),Table 1) results in 7-hydroxy-8-morpholine-methylcoumarine.

3.1. General Procedure

To an alcoholic solution containing 10 ml ethyl alcohol and 0.3 g paraformaldehide (0.01 mole), 0.9 g (0.01 mole) morpholine are added stepwise at the ambient temperature. Then 1.67 g 7-hydroxy-coumarine (0.01 mole) solved in 7 ml absolute ethanol is added. The reaction is then refluxed for two hours. Under cooling a crystalline product separates which is then purified from alcohol. In the IR spectrum the absorption bands for OH group (3188 cm^{-1}) lactone C= O (at 1 720 cm^{-1}) and for CN band (at 1 110 cm^{-1}) were found. The signals in NMR spectrum are given in Table 2.

^{1}H-NMR spectra were recorded on a JEOL-60 MHZ with THS as internal standard in $CDCl_3$ and DMSO-d_6.

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SINTEZA UNOR BAZE MANNICH DIN CLASA CUMARINELOR

(Rezumat)

S-au sintetizat șase baze Mannich plecînd de la 7-hidroxicumarina și 7-hidroxi-4-metilcumarina folosind drept amine : morfolina, metil-*n*-propilamina și metilbenzilamina. Compușii sînt caracterizați analitic și spectral (IR și RMN). Se analizează și acțiunea biologică a compușilor sintetizați.

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NEW DERIVATIVES OF N-(*p*-AMINOBENZOYL)-L-ASPARAGIC ACID WITH POTENTIAL ANTITUMOURAL ACTIVITY

BY

VALERIU ŞUNEL, ELENA IVAS and C. H. BUDEANU

1. Introduction

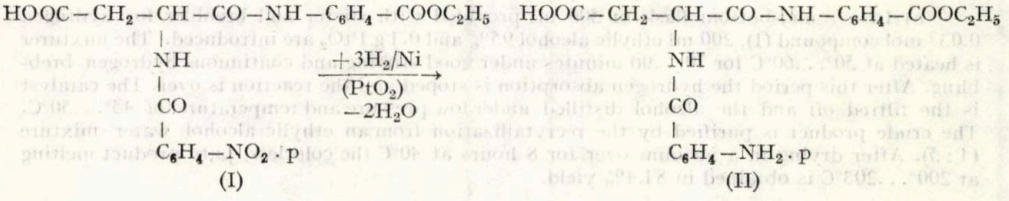
Some antagonists of aminoacids and alkylating compounds, such as N-mustards, inhibit the maligne tumour growth. Many investigators tried to decrease the extremely bigh toxicity of the N-mustard and to increase its therapeutic activity by substituting different aryl residues, aminoacids or peptides for the hydrogen atom. New N-mustards have been thus synthesized and applied in cancer chemiotherapy [1]. . .[5]. The *p*-aminobenzoic acid and some of its derivatives can also be used as carriers for the N-mustard group [6], [7].

In this connection, we synthesized new alkylating compounds containing the active group grafted on derivatives of the N-(*p*-nitrobenzoyl)-L-asparagic and N-(*p*-aminobenzoyl)-L-asparagic acids as well as on N-(*p*-aminobenzoyl)-L-asparagine [8]...[22].

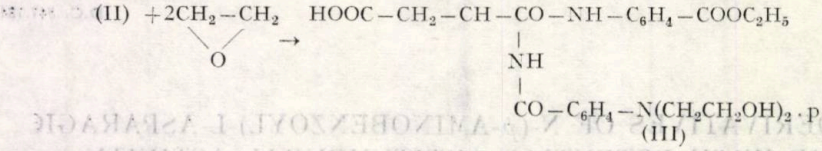
2. Results and Discussions

In the present paper a N-mustard with its active group grafted on a tripeptide consisting of a molecule of L-asparagic acid and two molecules of *p*-aminobenzoic acid, namely, the ethylic ester of the N-(*p*-aminobenzoyl)-α-DL-asparagyl-*p'*-aminobenzoic acid, has been synthesized and the correlation between the chemical structure and the biological activity studied.

The starting compound was the N-(*p*-nitrobenzoyl)-α-DL-asparagyl-*p'*-carbetoxyanilide (I) obtained by the decyclization of the 2-(*p*-nitrophenyl)-4-(β-carboxymethyl)-Δ^2-oxazolinone-5 by the ethylic ester of the *p*-aminobenzoic acid [23]. The nitro group in the N-(*p*-nitrobenzoyl)-α-DL-asparagyl -*p'*-carbetoxyanilide was reduced by gaseous hydrogen in alcoholic solution and in the presence of either platinum or nickel as a catalyst. The ethylic ester of the N-(*p*-aminobenzoyl)-α-DL asparagyl-*p'*-aminobenzoic acid (II) was thus obtained.

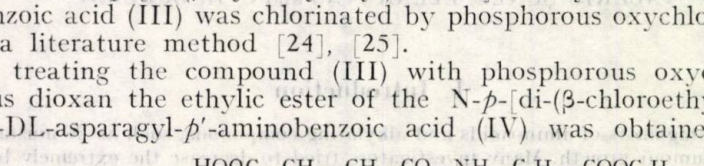


To convert the amino group into di-(β-chlorethyl)-amino one the corresponding di-(β-hydroxyethyl)-aminic (III) intermediate was synthesized by treating the amino compound (II) with ethylene oxide in diluted acetic acid medium.



By substituting the chlorine for the hydroxyl group in the di-(β-hydroxyethyl)-amino derivative was obtained. In this purpose the ethylic ester of the N-*p*-[di-(β-hydroxyethyl)-amino]-benzoyl-α-DL-asparagyl-*p'*-aminobenzoic acid (III) was chlorinated by phosphorous oxychloride according to a literature method [24], [25].

By treating the compound (III) with phosphorous oxychloride in anhydrous dioxan the ethylic ester of the N-*p*-[di-(β-chloroethyl)-amino]-benzoil-α-DL-asparagyl-*p'*-aminobenzoic acid (IV) was obtained.



The products (II)...(IV) were purified by the recrystallization from suitable solvents. The melting points are constant and the yields vary between 67.4% and 85.6%. The structure of the new compounds was elucidated by means of elemental analysis as well as IR spectral measurements [26]. These compounds show structural characteristics of a biological interest being able to act as antimetabolites or alkylating agents. The ethylic ester of the N-(*p*-aminobenzoyl)-α-DL-asparagyl-*p'*-aminobenzoic acid used as a carrier of the cytotoxic group within the tumoural tissue might confer a low toxicity and bighler selectivity to the compound (IV). This is probably so because in addition to the alkylating effect in the cancerous processes this derivative might also show an effect antagonistic to the N-(*p*-aminobenzoyl)-L-asparagic acid.

3. Experimental

3.1. N-(*p*-Nitrobenzoyl)-α-DL-asparagyl-*p'*-carbetoxyanilide (I)

It was obtained by the decyclization of 2-(*p*-nitrophenyl)-4-(β-carboxymethyl)-Δ^2-oxazolinone-5 by ethylic ester of the *p*-aminobenzoic acid [23].

3.2. Ethylic Ester of N-(*p*-Aminobenzoyl)-α-DL-asparagyl-*p'*-aminobenzoic Acid (II)

a) In a round-bottom flask of 500 ml provided with stirrer and brebbler for hydrogen 0.037 mol compound (I), 200 ml ethylic alcohol 95% and 0.1 g PtO_2 are introduced. The mixturer is heated at 50°. . .60°C for 70. . .90 minutes under good stirring and continuous hydrogen brebbling. After this period the hydrogen absorption is stoped and the reaction is over. The catalyst is the filtred off and the alcohol distilled under low pressure and temperature of 45°. . .50°C. The crude product is purified by the recrytallization from an ethylic alcohol water mixture (1 : 5). After drying in a vacuum over for 8 hours at 40°C the colorless, pure product melting at 200°. . .203°C is obtained in 81.4% yield.

b) 0.037 mol compound (I), 200 ml anhydrous ethylic alcohol, 1 g Ni/Reney are introduced into on autoclave. The reaction mixture is heated at 50°...55°C for 75...85 minutes while hydrogen is continuously brebbled. The catalyst is filtred off and the alcohol distilled under low pressure at 50°...55°C. The crude product is dissolved in a boiling ethylic alcohol—water mixture (1 : 3) there charcoal added and filtered. Colorless crystals separate by cooling which are filtered off and dryied melting 200°...202°C. The reaction yield 85.6%.

Analyses ($C_{20}H_{21}N_3O_6$)	C%	H%	N%
Calculated :	60.15	5.26	10.52
Found :	60.37	5.34	10.70
	60.46	5.37	10.80

The IR spectrum (KBr): 3140...3440 cm^{-1}, wide band with maxima at 3245 cm^{-1}, 3350 cm^{-1} ν_{N-H}; 1645 cm^{-1} $\nu_{C=O}$ amidic; 1730 cm^{-1} $\nu_{C=O}$; 1152, 1170, 1195 cm^{-1} ν_{C-O-C}; 795 cm^{-1} 812 cm^{-1} ν_{C-H} aromatic.

3.3. Ethylic Ester of N-*p*-[di-(β-Hydroxyethyl)-amino]-benzoyl α-DL asparagyl-*p'*-aminobenzoic Acid (III)

In a round-bottom flask provided with stirrer a suspension of 0.02 mol ethylic ester of the N-(*p*-aminobenzoyl)-α-DL-asparagyl-*p'*-aminobenzoic acid (II) in 100 ml distilled water and 80 ml glacial acetic acid is prepared and 40 ml ethylen oxide are added. The mixture is maintained for 24 hours at the room temperature under stirring and then neutralized by sodium bicarbonate. The oil product formed is separated from the aqueous solution, solved in ethylic alcohol, dried on anhydrous sodium sulphate and ther filtered. The alcohol in excess is distilled under low pressure and temperature of 40°...45°C up to a volume of 10...15 ml. A viscous mass separates by the cooling which gives a colorless crystalline product melting at 70°...72°C by the recrystallization from a benzene—ethylic ether mixture (1 : 2). Reaction yield 71.4%.

Analyses ($C_{24}H_{29}N_3O_8$)	C%	H%	N%
Calculated :	59.13	5.95	8.62
Found :	59.38	6.17	8.96
	59.44	6.19	9.06

The IR spectrum (KBr): 3366 cm^{-1}, 3460 cm^{-1} $\nu_{N=H}$; 1732 cm^{-1} $\nu_{C=O}$ ester; 1620 cm^{-1} $\nu_{C=O}$ amidic; 1162 cm^{-1}, 1190 cm^{-1} ν_{C-O-C}; 1300 cm^{-1} $_{C-N}$; 1070 cm^{-1} ν_{C-O-H}; 865 cm^{-1} ν_{C-H} aromatic.

3.4. Ethylic Ester of N-*p*-[di-(β-Chloroethyl)-amino]-benzoyl α-DL asparagyl *p'*-aminobenzoic Acid (IV)

Into a round-bottom flask provided with reflux condenser 0.006 mol ethylic ester of N-*p*-[di-(β-hydroxyethyl)-amino]-benzoyl-α-DL-asparagyl-*p'*-aminobenzoic acid (III), 3.5 ml phosphorous oxychloride and 50 ml anhydrous dioxan are introduced. The mixture is heated at 70°...80°C on a water bath for 90 minutes. After cooling the reaction product obtained as an homogeneous solution is poured on 50 g of crashed ice. A concentrated solution of sodium acetate is then added up to the pH=2.5 and heated for 45 minutes at 40°...45°C when a solid product separates. The precipitate is filtered and dried in an oven at the temperature of 50°C. The crude product is solved in warm chloroform, treated with charcoal and filtered. After benzene addition a solid bright-yellow product separates from the filtrate. The product thus purified and dried melts at 175°...177°C. The reaction yield is 67.4%.

Analyses ($C_{24}H_{27}Cl_2N_3O_6$)	C%	H%	Cl%	N%
Calculated :	54.96	5.15	13.54	8.01
Found :	55.16	5.46	13.95	8.15
	55.22	5.37	14.02	8.22

The IR spectrum (KBr): 3308 cm^{-1}, 3334 cm^{-1} ν_{N-H}; 1734 cm^{-1} $\nu_{C=O}$ ester; 1630 cm^{-1} $\nu_{C=O}$ amidic; 1205 cm^{-1} ν_{C-O-C}; 1320 cm^{-1} ν_{C-N}; 870 cm^{-1} ν_{C-H} aromatic; 720 cm^{-1} ν_{C-Cl}.

4. Conclusions

Three new derivatives (II)...(IV) of the N-(*p*-aminobenzoyl)-L-asparagic acid have synthesized.

A new N-mustard (IV) having the active group grafted on a tripeptide was obtained by the chlorination of the ethylic ester of the N-*p*-[di-(β-hydroxyethyl)-amino]-benzoyl-α-DL-asparagyl-*p'*-aminobenzoic acid with phosphorous oxychloride.

The structure of the obtained products was elucidated by means of elemental analysis and IR spectral measurements.

The compounds (II)...(IV) shaw structural characteristics of a biological interest.

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NOI DERIVAȚI AI ACIDULUI N-(*p*-AMINOBENZOIL)-L-ASPARAGIC CU ACTIVITATE ANTITUMORALĂ POTENȚIALĂ

(Rezumat)

În scopul obținerii de noi substanțe cu activitate antitumorală potențială s-a sintetizat esterul etilic al acidului N-*p*-[di-(β-cloretil)-amino]-benzoil-α-DL-asparagil-*p'*-aminobenzoic prin înlocuirea grupelor hidroxilice din compusul di-(β-hidroxietil)-aminic corespunzător cu clor. Alchilantul prezintă caracteristici structurale de interes biologic.

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D.C. 678.746.22 — 136.22

COPOLYMERS

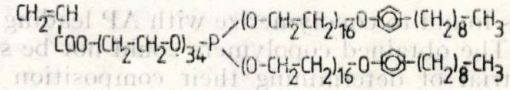
IV. STUDY ON COPOLYMERIZATION OF VINYL ACETATE WITH POLYETHYLENEGLYCOL-DINONYL-PHENOXY-POLYETHYLENEGLYCOL-PHOSPHATE ACRYLATE

BY

N. ASANDEI, M. NICU, C. ȘINDILARU, VIORICA NICU and CEZAR RICINSCHI

1. Introduction

The polyethyleneglycol-dinonyl—phenoxy-polyethyleneglycol-phosphate acrylate (AP) monomer has been recently synthesized

(1) 

Its structure was confirmed by the IR spectrum (Fig. 1) and in a certain extent by the NMR spectrum (Fig. 2). In both spectra the absorptions and the signals characteristic of the functional groups in AP are evidenced. The proton integral is not correlated perfectly with the proton proportions indicated by the formula (1).

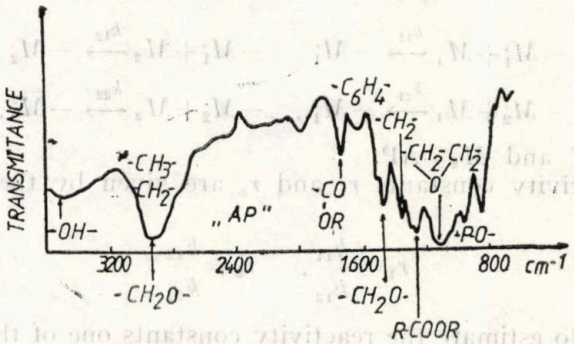


Fig. 1. — The IR spectrum of AP.

The vinyl acetate (AV) and AP are termonomers in the terpolymerization with acrylonitrile (AN). In order to approach the composition aspects of the terpolymers the AV—AP binary system was also studied.

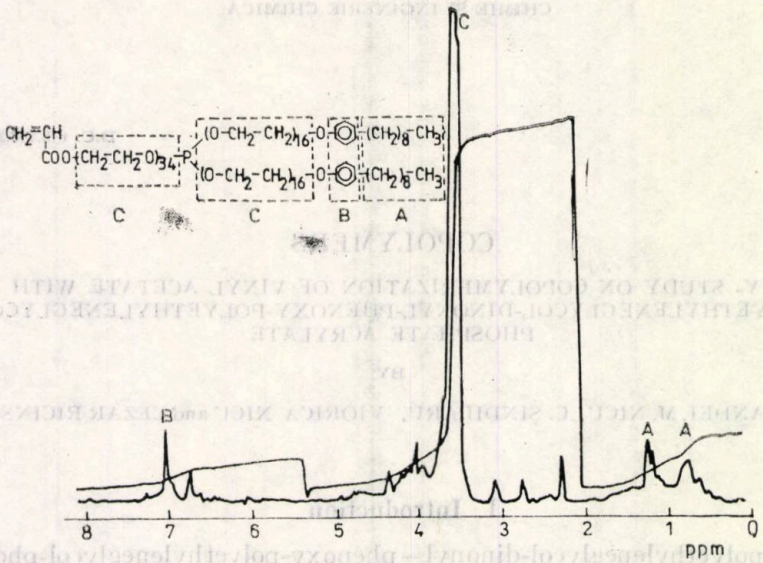


Fig. 2. — The NMR spectrum of AP.

The AV was found to copolymerize with AP leading to viscous brown-coloured liquids. The obtained copolymers could not be separated from the monomers. The trial of determining their composition by IR and NMR spectral measurements has failed. Consequently, the AV and AP copolymerization was studied theoretically.

2. Estimation of Copolymerization Constants

The AP was assumed to copolymerize with AV according to the M a y o—L e w i s model [4], like its similar monomers [1] ... [3]:

$$(2)\qquad \begin{aligned} -M_1^{\cdot}+M_1 &\xrightarrow{k_{11}} -M_1^{\cdot}, \quad -M_1^{\cdot}+M_2 \xrightarrow{k_{12}} -M_2^{\cdot}, \\ -M_2^{\cdot}+M_1 &\xrightarrow{k_{21}} -M_1^{\cdot}, \quad -M_2^{\cdot}+M_2 \xrightarrow{k_{22}} -M_2^{\cdot}, \end{aligned}$$

where M_1=AV and M_2=AP.

The reactivity constants r_1 and r_2 are given by the rate constant ratios:

$$(3)\qquad r_1=\frac{k_{11}}{k_{12}}, \qquad r_2=\frac{k_{22}}{k_{21}}.$$

In order to estimate the reactivity constants one of the availabilities of the $Q-e$ scheme was used. The Q parameter depends on the resonance effects in the either monomer molecule or radical while the e is determined by the radical and monomer polarities. The Q and e parameters of AP were calculated based on the reactivity constants found experimentally for the AN—AP system by using the relationships [5]:

(4) $$e_2 = e_1 \pm (-\ln r_1 r_2)^{1/2}, \quad Q_2 = Q_{1/r_1} \exp\left[-e_1(e_1 - e_2)\right],$$

where indices 2 and 1 refer to AP and AN, respectively :

$$Q_1 = 0.6, \quad e_1 = 1.2, \quad r_1 = 15, \quad r_2 = 0.3.$$

By calculation $Q_2 = 1.74$ and $e_2 = 2.42$ were found which places AP among the monomers with double bond strongly positively polarized having a pronounced tendency to stabilization by resonance.

By using the above values as well as the relations given below, where the index 1 denotes the AV, the reactivity constants r_1 and r_2 for the AV—AP system were calculated :

(5) $$r_1 = \frac{Q_1}{Q_2} \exp\left[-e_1(e_1 - e_2)\right], \qquad r_2 = \frac{Q_2}{Q_1} \exp\left[-e_2(e_2 - e_1)\right].$$

For vinyl acetate the parameters have the values : $Q_1 = 0.026$ and $e_1 = -0.22$. By performing the calculations $r_1 = 0.008$ and $r_2 = 0.11$ were found.

3. Composition Diagram

By taking into account the above reactivity constants the following composition equation for the system under study can be advanced :

(6) $$n = \frac{0.008x^2 + x}{0.11 + x},$$

where x is the ratio of the molar concentrations of the comonomers in substratum (M_1, M_2), while n denotes the ratio of the molar fractions of the comonomers in copolymer (m_1, m_2).

By means of the equation (6) the composition diagram depicted in Fig. 3 was calculated.

The composition diagram shows an azeotropic point at about 53% M_2. The copolymers synthesized from substrata containing up to 53% M_2 are richer in AP, and the subsequent composition interval shows a concentration higher in copolymer than of AP although the AV concentration in substratum is lower.

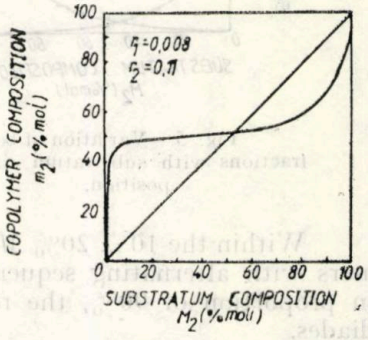


Fig. 3.—Composition diagram of the AV—AP system.

4. Structure of Copolymers

4.1. Variation of Substratum and Copolymer Compositions with Conversion

The variation of the substratum and copolymer compositions was calculated as a function of conversion for a AV—AP system composition equivalent to that for a terpolymerization checked industrially. The obtained results are illustrated in Fig. 4.

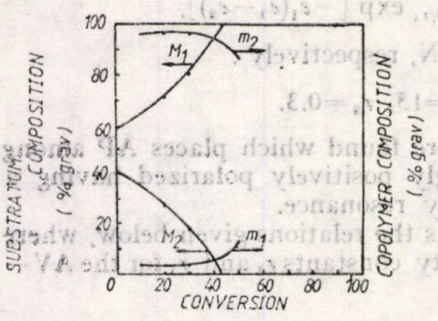


Fig. 4. — Composition variation with conversion.

Due to its much higher reactivity AP consumes from the reaction medium when the process conversion attains 40 ... 50%. The compositions of both substrata and copolymers are significantly influenced by conversion.

4.2. Sequence in Copolymers

The sequence in copolymers was appreciated by means of the bond fractions and addition probabilities. The bond fractions were calculated by means of the defining relationships [4] :

$$f_{11}=\frac{r_1 x}{r_1 x+2+r_2/x}, \qquad f_{22}=\frac{r_2/x}{r_1 x+2+r_2/x},$$

$$f_{12}=f_{21}=\frac{1}{r_1 x+2+r_2/x}. \tag{7}$$

The variation of bond fractions is depicted as a function of the substratum composition (Fig. 5) and of the copolymer composition (Fig. 6).

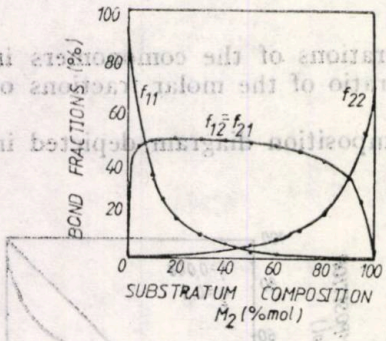


Fig. 5. — Variation of bond fractions with substratum composition.

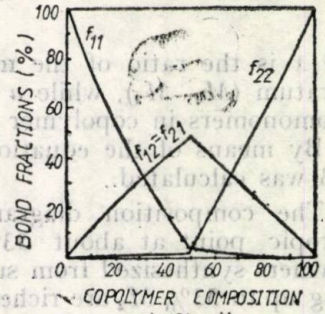


Fig. 6. — Variation of bond fractions with copolymer composition.

Within the 10 ... 20% M_2 composition range of substratum the copolymers with alternating sequences are seen to form predominantly, namely in proportion of 90%, the remaining content consisting in homogeneous diades.

The fact deserves mention that the AV and AP contents in terpolymers correspond to the composition range assuring the formation of alternating copolymers.

The addition probabilities were calculated by means of the relationships [4] :

$$(8) \qquad P_{11}=\frac{r_1 x}{r_1 x+1}, \quad P_{12}=\frac{1}{r_1 x+1}, \quad P_{21}=\frac{x}{r_2+x}, \quad P_{22}=\frac{r_2}{r_2+x}.$$

The variation of addition probabilities in function of the substratum composition (Fig. 7) would indicate crossing addition for a wide composition range (10 ... 90% M_2) which results in formation of an alternating copolymer.

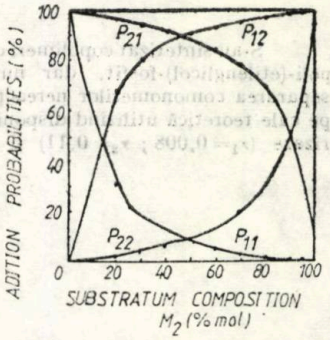


Fig. 7. — Variation of addition probabilities as a function of substratum composition.

5. Conclusions

By studying the copolymerization of AV with AP the following conclusions have been drawn :

1. The reaction of AV with AP results in formation of copolymers which can be neither separated from the unreacted monomers nor analysed for their composition.

2. By means of the Q and e parameters the reactivity constants $r_1 = 0.008$ and $r_2 = 0.11$ were estimated.

3. The AV—AP copolymers are of the statistical type with a pronounced tendency to alternation.

4. The composition of both substrata and copolymers is strongly affected by the conversion.

5. The AV—AP mixtures used in industrial terpolymerizations are situated within substratum composition range leading principally to alternating copolymers.

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Polytechnic Institute, Jassy, Department of Organic and Macromolecular Chemistry and Technology

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COPOLIMERI

IV. Studiul copolimerizării acetatului de vinil cu acrilatul de poli-(etilenglicol)-dinonil-penixi-poli-(etilenglicol)-fosfit

(Rezumat)

S-au sintetizat copolimeri din acetat de vinil și acrilatul de poli-(etilenglicol)-dionil-penixi-poli-(etilenglicol)-fosfit, dar nu s-au putut analiza compoziționa1 deoarece nu s-a reușit separarea comonomerilor nereacționați, motiv pentru care studiul copolimerizării s-a efectuat pe cale teoretică utilizînd disponibilitățile schemei $Q-e$. S-au calculat constantele de copolimerizare ($r_1 = 0{,}008$; $r_2 = 0{,}11$) și compoziția secvențială a copolimerilor.

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D C. 678.742.2

STRUCTURAL CHARACTERIZATION OF SOME SULFONATED ESTERS OF POLY(ETHYLENE OXIDE)

BY

LILIANA D. PETROVA, I. DRUŢĂ and I. I. NEGULESCU

1. Introduction

The earliest reports on the polymerization of ethylene oxide were made by W u r t z in the second half of the 19th century [1]...[3], but fundamental and extensive studies were carried out by S t a u d i n g e r *et al.* fifty years later [4], [5] for the purpose of synthesizing model cellulose substance by polymerizing epoxides with various kinds of anionic and cationic initiators. However, only in 1950's the petrochemical industry began to supply ethylene oxide, propylene oxide, epichlorohydrin and other epoxides in large quantities. Using these epoxides, low or medium molecular weight polymers were manufactured and used as surfactants, water-soluble lubricants for rubber molds, textile fibers, plasticizers, adhesives, printing inks, paper coatings, components of cosmetics and pharmaceuticals, and as raw materials for the production of urethane foams, elastomers, coatings, etc. [6].

The epoxides are unique among cyclic ethers ; their polymerization may proceed by an anionic, cationic, or a coordinate mechanism [7]. All three mechanisms are not equally important, nor have all a commercial significance. Still all mechanisms have been reviewed extensively [8]. A number of studies of the kinetics and mechanism of the base catalyzed reaction of epoxides with phenolic alcohols have served as background for the polyaddition investigations [6]. These studies showed that both the alcoohol and alkoxide participate in the rate determining step and subsequently a termolecular mechanism was proposed, which is particularly responsible for the rather low molecular weight of the polymers.

On the one hand, the molecular weight distribution of polyalkylene oxides is important because it affects the characteristics of these polymers and, on the other, the solubility of oligomeric polyepoxides, as well as their service properties, can be controlled by chemical modifications carried out mainly through terminal hydroxy groups.

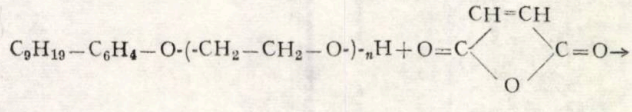
Therefore the aim of the present paper is to determine the chemical structure and molecular weight distribution of some sulfonated maleic esters of poly(ethylene oxide) obtained by polyethoxylation of nonyl phenol.

2. Experimental

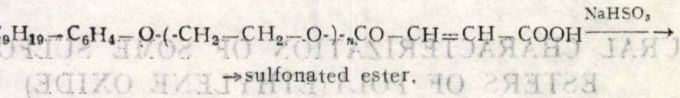
Oligomers of poly(ethylene oxide) were synthesized by basic ethoxylation of nonyl phenol :

(1) $$C_9H_{19}-C_6H_4-OH + n\underset{\diagdown O \diagup}{CH_2-CH_2} \xrightarrow{KOH} C_9H_{19}C_6H_4O\text{-}(\text{-}CH_2-CH_2-O\text{-})_n H$$

The average polyaddition degree, n, varied between 3 and 30 depending on reaction conditions [9]. The obtained oligomers were esterified with maleic anhydride and the formed esters were subsequently reacted with $NaHSO_3$ [10] :



(2)



Spectral data were recorded using an IR Specord (DDR) spectrophotometer and JEOL 60 MHz and Bruker 100 MHz NMR spectrometers. The molecular weight distribution was determined by GPC (Waters 200) at 20°C using THF as eluent.

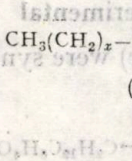
3. Results and Discussion

The following aspects regarding the structure of sulfonated materials obtained according to eq. (2) were elucidated in the present work : a) the structure of the starting alkyl phenol ; b) the place of the $-SO_3H$ group in the maleic rest. Additionally the change of molecular weight distribution of the oligomers obtained in eq. (1) with the degree of ethoxylation was observed.

The most probable structure and place of the alkyl group in nonyl phenol were obtained from IR and NMR spectra of this derivative. Thus, the two bands at 1 760 and 1 882 cm^{-1}, corresponding to the aromatic absorption from 810 ... 830 cm^{-1} (Fig. 1) is a strong indication that the nonyl radical is positioned in *para*.

The NMR spectrum of the same derivative confirms the *para* position of the alkyl substituent in the domain of aromatic protons : a pair of *ortho* protons centered at 6.64 ppm and a multiplet of the protons positioned in *metha* as regards the OH group determined by sterical influences of the neighbouring alkyl radical.

The structure of the nonyl radical is suggested by the nature and ratio of saturated protons from $\delta = 0.4 \ldots 2.0$ ppm as it follows : a) the absence of any signal between $\delta = 2 \ldots 3$ ppm indicates that the carbon atom adjacent to the aromatic ring is completely substituted with alkyl radicals and b) the ration between CH_2 protons from $\delta = 0.95 \ldots 1.82$ ppm and CH_3 protons from $\delta = 0.4 \ldots 0.95$ ppm, close to 10 : 9, points to a repartition of these groups as follows :



where: x, y, $z = 0 \ldots 5$, $x+y+z=5$.

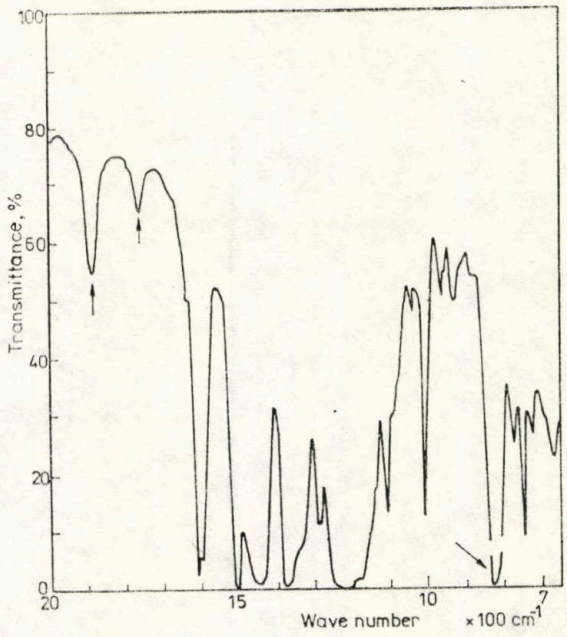


Fig. 1. — IR spectrum of $C_9H_{19}-C_6H_4-OH$; film on KBr pellet.

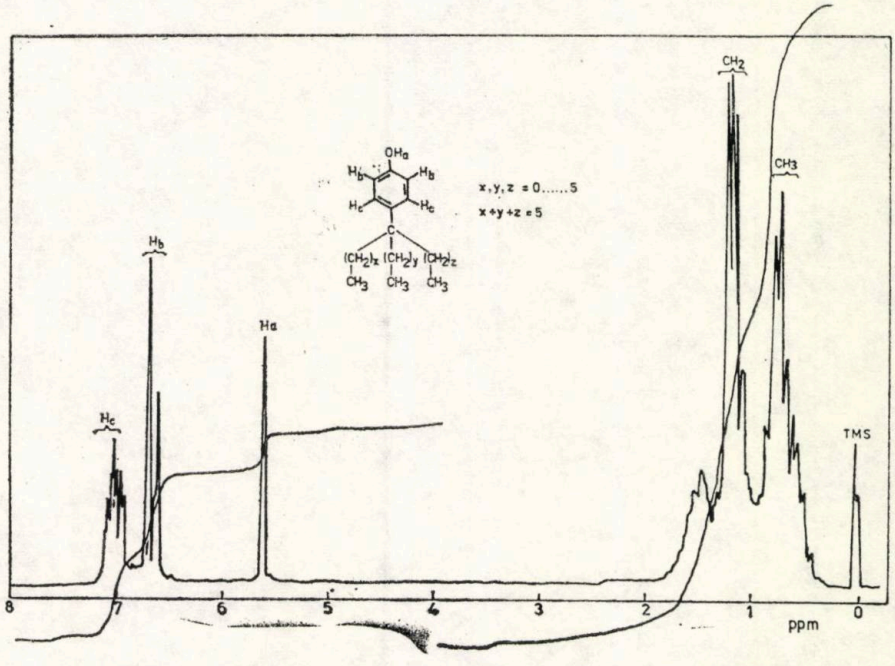
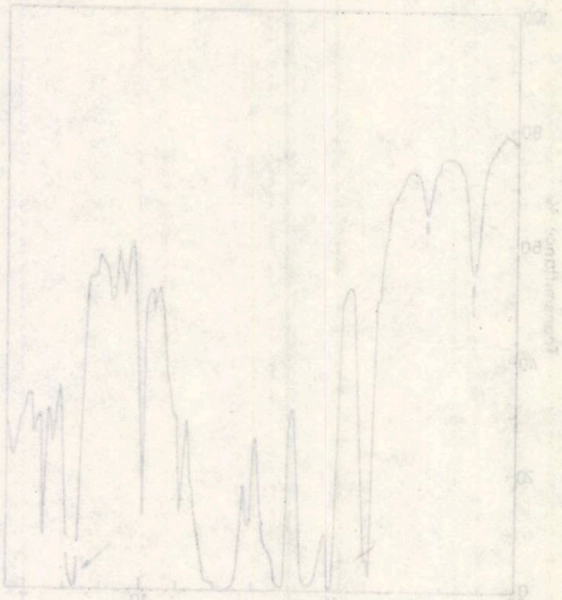
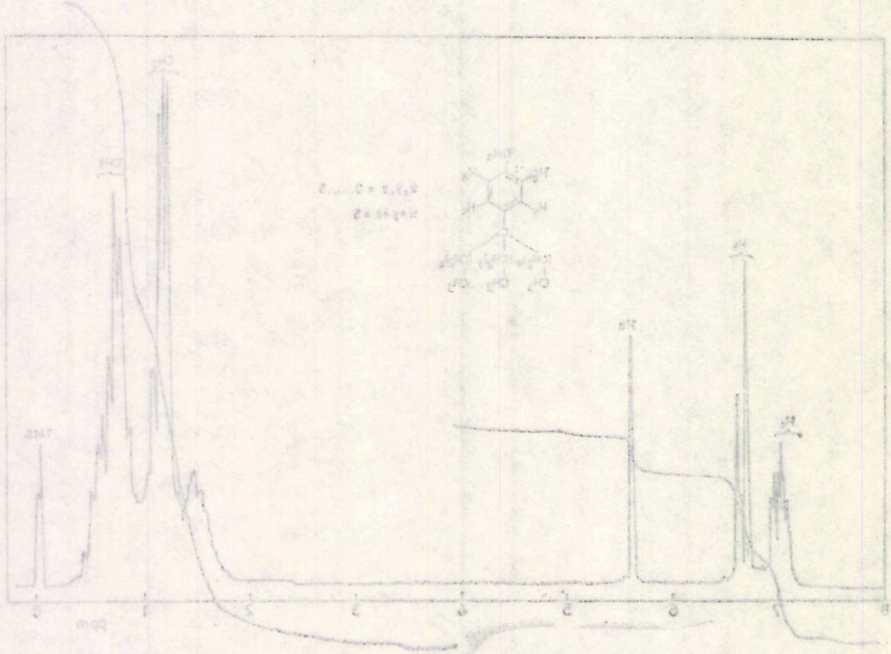
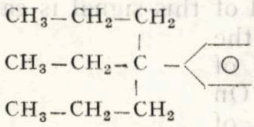


Fig. 2. — H^1-NMR spectrum (100 MHz) of $C_9H_{19}-C_6H_4-OH$ in $CDCl_3$.





Consequently one of the isomers of these alkyl phenols can be written as :



Considering now the place of the $-SO_3H$ group in the maleic rest of the esterified polyethoxylated alkyl phenol, it can be added nucleophylically either in α or in β positions, giving structure :

(I) $C_9H_{19}-C_6H_4-O(CH_2-CH_2-O-)_n CO-\underset{\underset{SO_3^{\ominus}}{|}}{CH}-CH_2-COO^{\ominus}$

or

(II) $C_9H_{19}-C_6H_4-O(CH_2-CH_2-O-)_n CO-CH_2-\underset{\underset{SO_3^{\ominus}}{|}}{CH}-COO^{\ominus}$

respectively.

A simple molecular orbital calculation (HMO) showed a higher probability for formation of structure (II) [11]. In order to prove it experimentally, the NMR signals of CH_2 protons from ethyl succinate and its sodium salt (formed *in situ* from ester + $NaHCO_3$) were compared (Fig. 3). The

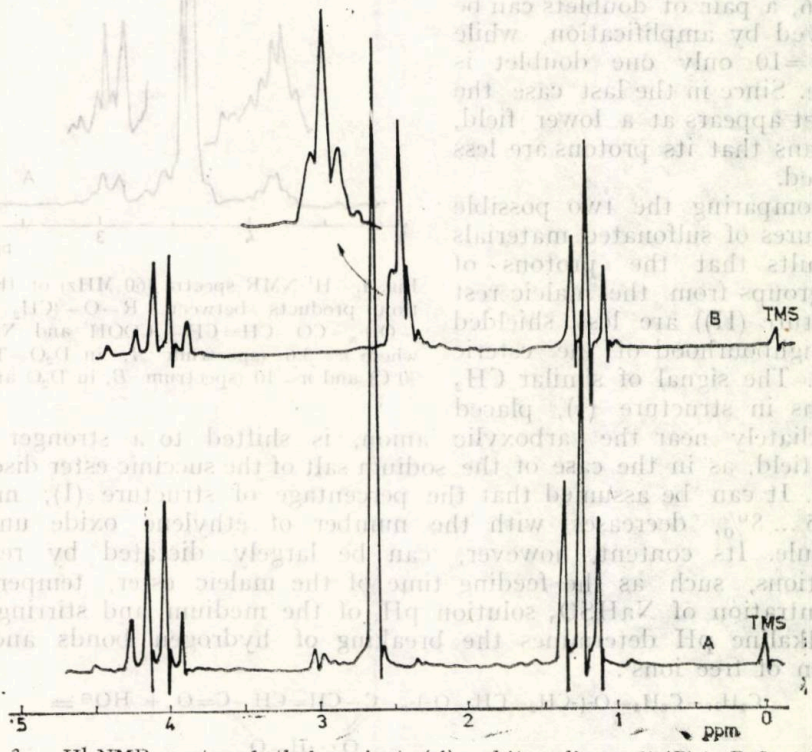


Fig. 3. — H^1-NMR spectra of ethyl succinate (*A*) and its sodium salt (*B*) in D_2O at 20°, 60 MHz.

two CH_2 groups of the ester give a signal at $\delta = 2.7$ ppm while the same groups appear in the case of sodium salt at $\delta = 2.48$ ppm as a splitted triplet. The shifting to a stronger field of this signal is caused by the annihilation of the inductive effect $-I$ of the $-COOH$ group by formation of carboxylate anion $-COO^{\ominus}$. On the other hand, the analysis of NMR spectra of a series of sulfonated materials obtained according to eq. (2), where $n = 3,5,6,7$ and 10, showed that the protons signals from the $-CH_2-\underset{|}{CH}-$ group, which appear as a doublet at $\delta = 3.12$ ppm (CH_2) and a triplet at $\delta = 4.25$ ppm (CH), were shifted to a less intense magnetic field as the number of ethylene oxide units in the molecule increased [12]. At the same time the doublet became more distinct at higher n values. In Fig. 4, for $n = 3.6$, a pair of doublets can be observed by amplification, while for $n = 10$ only one doublet is visible. Since in the last case the doublet appears at a lower field, it means that its protons are less shielded.

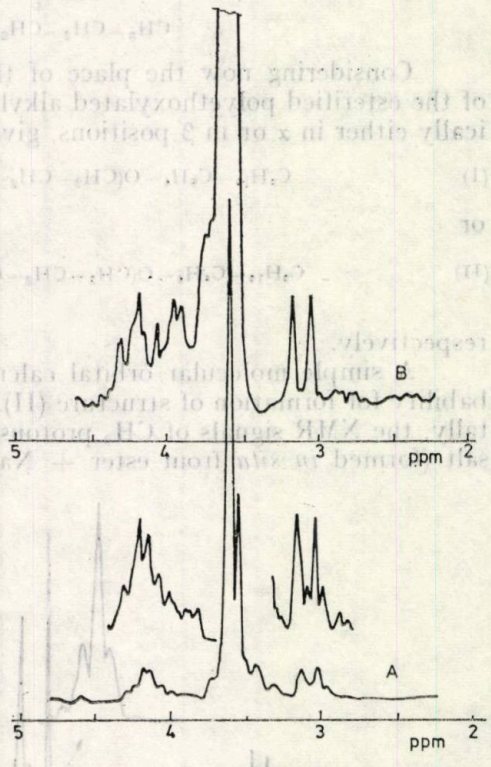


Fig. 4. — H^1-NMR spectra (60 MHz) of the reaction products between $R-O-(CH_2-CH_2-O-)_n-CO-CH=CH-COOH$ and $NaHSO_3$, where $n = 3.6$ (spectrum A, in D_2O + THF at 70°C) and $n = 10$ (spectrum B, in D_2O at 70°C).

Comparing the two possible structures of sulfonated materials it results that the protons of CH_2 groups from the maleic rest (structure (II)) are less shielded by neighbourhood of the esteric group. The signal of similar CH_2 protons in structure (I), placed immediately near the carboxylic anion, is shifted to a stronger magnetic field, as in the case of the sodium salt of the succinic ester discussed above. It can be assumed that the percentage of structure (I), maximum 5 ... 8%, decreases with the number of ethylene oxide units in molecule. Its content, however, can be largely dictated by reaction conditions, such as the feeding time of the maleic ester, temperature, concentration of $NaHSO_3$ solution pH, of the medium and stirring [12]. An alkaline pH determines the breaking of hydrogen bonds and formation of free ions:

$$C_9H_{19}-C_6H_4-O-(-CH_2-CH-O-)_n-C(=O\cdots H-O)-CH=CH-C=O + HO^{\ominus} \rightleftharpoons$$
$$\rightleftharpoons C_9H_{19}-C_6H_4-O-(-CH_2-CH_2-O-)_n-CO-CH=CH-COO^{\ominus} + H_2O \quad (3)$$

The last parameter, if too slow, can allow the apparition of some agglomerates having an external ionic layer, which assures the hydrophylicity, that may contain important amounts of unreacted ester.

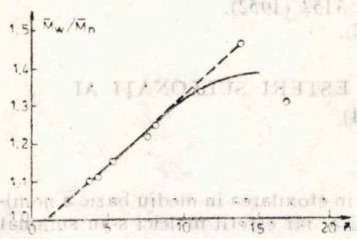


Fig. 5.—The dependence of $\bar{M}_w/\bar{M}_n$ ratio on the average number of ethylene oxide units in $C_9H_{19}-C_6H_4-O-(CH_2-CH_2-O-)_nH$ oligomers.

As regards the distribution of molecular weight of these oligomers, it depends on the polyaddition conditions and, theoretically, it can be computed if certain assumptions concerning the relative reactivities of the starting alcohol and its epoxide adduct are introduced [13] ... [15]. As seen in Fig. 5, the ratio $\bar{M}_w/\bar{M}_n$ value determined by GPC strongly depends on the average number of encatenated monomer units, i.e. the larger the n, the higher the $\bar{M}_w/\bar{M}_n$ ratio is obtained. This result is in good agreement with the polyaddition theory which states that, at a certain time, species of various molecular weight are present in the reaction system [7].

4. Conclusions

The analysis of a series of sulfonated maleic esters of poly(ethylene oxide) oligomers obtained by polyethoxylation of nonyl phenol revealed that:

a) the alkyl rest (C_9H_{19}) is placed in *para* position and has a substituted structure of quaternary type;

b) the $-SO_3H$ group is attached mostly to the α carbon atom as regards the carboxylic group;

c) the $\bar{M}_w/\bar{M}_n$ ratio increases with the number of ethylene oxide units up to $n \sim 15$.

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CARACTERIZAREA STRUCTURALĂ A UNOR ESTERI SULFONAȚI AI POLI(ETILEN-OXIDULUI)

(Rezumat)

S-au sintetizat o serie de oligomeri de polietilenoxid prin etoxilarea în mediu bazic a nonilfenolului. Oligomerii au fost apoi tratați cu anhidridă maleică iar esterii maleici s-au sulfonat cu $NaHSO_3$.

Analizele au arătat că restul alchil C_9H_{19} din fenolul inițial are o structură cuaternară, fiind plasat în poziția *para*. Gruparea sulfonică se atașează în principal atomului de carbon α față de gruparea carboxilică.

Indicele de polimolecularitate a oligomerilor crește odată cu masa moleculară pînă la aproximativ 15, stabilindu-se la o valoare $\overline{M}_w/\overline{M}_n = 1{,}5$.

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УДК 54–92

СМЕСИ ПОЛИМЕРОВ

I. ФИЗИКО-МЕХАНИЧЕСКИЕ СВОЙСТВА

М. РУСУ, С. ПЕТРОВАН, М. ЛУНГУ и Г. АДАМЕСКУ

1. Введение

В результате термомеханической обработки смеси полимеров получаются, в большинстве случаев, продукты с более низкими характеристиками по сравнению с продуктами, получающимися при отдельной обработке каждого типа полимера. Такое поведение является обычно результатом несовместимости компонентов, составляющих подвергаемую обработке смесь.

Несовместимые полимеры характеризуются высоким межфазным натяжением и отсутствием межфазной агдезии, что затрудняет диспергирование компонентов до молекулярного уровня ; вследствие этого, получающиеся смеси являются гетерогенными. Гетерогенная структура таких смесей и отсутствие межфазной адгезии определяет более низкие значения их физико-механических показателей сравнительно с физико-механическими показателями взятых компонентов. Вследствие этого, в последние годы возрос интерес к исследованиям, целью которых является улучшение физико-механических свойств гетерогенных систем полимеров, в особенности систем, состав которых близок к составу смесей, получаемых при разделении пластмассовых отходов из твёрдных городских отбросов.

Проведённые исследования показали, что заметное улучшение основных свойств смесей несовместимых полимеров может быть получено путём введения в систему агентов, улучшающих межфазную адгезию, известных под названием агентов по улучшению совместимости [1].

В качестве таких агентов, наиболее часто используются блок-сополимеры и привитые сополимеры, боковые цепи или блоки которых имеют большую длину. Наиболее эффективное действие по улучшению совместимости оказывают сополимеры (блок-сополимеры или привитые сополимеры), у которых имеются сегменты, идентичные с химической точки зрения с полимерами, совместимость которых требуется обеспечить. Сегменты сополимеров, используемых в качестве агентов по улучшению совместимости, проникают через межфазную поверхность и обеспечивают сцепление фаз [1], [2].

Эффекты по улучшению совместимости получаются как в случае смешиваемости различных сегментов блок-сополимеров или привитых сополимеров только с одной из фаз системы, так и в случае локализации агента по улучшению совместимости на поверхности раздела фаз, что обеспечивает увеличение адгезии между фазами [1] ... [9].

Настоящее исследование ставит своей целью показать влияние добавок сополимера этилена и винилацетата на основе физико-механических свойства двойных и тройных смесей на основе полиэтилена, полистирола и поливинилхлорида, с тем, чтобы установить, в какой мере этот сополимер может быть использован в качестве агента по улучшению совместимости вышеуказанных систем.

2. Экспериментальная часть

Для проведения данного исследования использовались следующие мартериалы :

а) полиэтилен высокого давления (ПЭВД) типа „A23 B/035“, производимого нефтехимическим комбинатом Питешть (Румыния) (индекс текучести=1,85 г/10 мин., плотность=0,9221 г/см³) ;

б) полистирол (ПС), суспензия, производимый нефтехимическим комбинатом Борзешть (Румыния) (характеристическая вязкость в бензоле при 20°C=1,28) ;

в) поливинилхлорид (ПВХ), суспензия, типа „драй бленд“, производимый нефтехимическим комбинатом Борзешть (Румыния) (κ=68, характеристическая вязкость в тетрагидрофуране при 20°C=0,51) ;

г) сополимер этилена с винилацетатом (СЭВА), типа ЛЕВАПРЕН 450 (45% винилацетата, характеристическая вязкость в бензене при 20°C= =1,44).

С использованием вышеуказанных трёх основных компонентов (ПЭВД, ПС, ПВХ), были осуществлены двойные и тройные смеси с добавкой СЭВА и без этой добавки. Процентное содержание добавляемого СЭВА принималось равным 10, 20 и 30% от общего количества смеси.

Перемешивание компонентов проводились на лабораторных вальцах Берстоффа при температурах от 110° до 180°C и продолжительности вальцевания 10 мин.; полученные смеси спрессовывались в плиты толщиной 1 и 4 мм (при давлении 175 кгс/см² и температуре 170°C, в течение 10 мин.) ; из этих листов получили путём вырубания образцы, необходимые для определения прочности при растяжении, удлинения при разрыве (по стандарту СТАС 6 642/62) и ударной прочности по Изоду (по стандарту СТАС 7 310/65).

3. Результаты и их обсуждение

Двойные и тройные смеси на основе ПЭВД, ПС и ПВХ известны как несовместимые системы [10] ... [12], а их физико-механические свойства

Таблица 1

Состав и свойства смесей ПЭВД, ПС и ПВХ

Пор. но. испытания	Состав смесей, %			Свойства смесей		
	ПЭВД	ПС	ПВХ	Прочность при растяжении кгс/мм²	Удлинение при разрыве %	Ударопрочность по Изоду кгс. см/см
1	100	—	—	0,945	480	48,5
2	66,5	33,4	—	0,515	5,0	6,5
3	33,4	66,6	—	0,20	0,4	5,0
4	—	100	—	3,45	0,4	2,9
5	—	66,6	33,4	1,625	0,5	2,3
6	—	33,4	66,6	1,75	0,5	1,9
7	—	—	100	5,60	8,0	6,0
8	33,4	—	66,6	0,80	0,5	29,0
9	66,6	—	33,4	0,695	8,0	10,0

уступают свойствам взятых полимеров, что отражается данными таблицы 1.

Из рассмотрения этих данных видно, что для всех исследованных смесей, такие физико-механические характеристики, как прочность при растяжении, удлинение при разрыве и ударопрочность по Изоду, сильно отклоняются от „правила аддитивности". Значения этих характеристик уменьшаются по мере приближения к середине интервала состава смеси, при этом всегда наблюдается существование минимума. В случае двойных систем, наименьшие значения характеристик располагаются вблизи середины интервала (где оба компонента содержатся в равных частях), но нет строгого соблюдения этого правила ; для прочности при растяжении и удлинения при разрыве, положение минимума смещено в сторону компонента с меньшим значением характеристики.

Тройная смесь, в которой три основные полимера содержатся в равных частях, характеризуется более низким значением ударной прочности по Изоду сравнительно с двойными смесями, а удлинение при разрыве принимает близкие к нулю значения. Прочность при растяжении для этой смеси выше чем для двойных систем на основе ПЭВД—ПС и ПЭВД—ПВХ, но ниже чем для двойных систем на основе ПС и ПВХ.

Для всех исследованных смесей из ПЭВД, ПС и ПВХ, значения физико-механических характеристик ниже соответствующих значений для исходных высокомолекулярных соединений ; это объясняют гетерогенной структурой этих систем и отсутствием межфазной адгезии [11]. Отсутствие адгезии препятствует передаче натяжения от одной фазы к другой ; поверхность контакта между фазами представляет собой натуральную трещину, легко распространяющуюся под действием нагрузки.

В случае тройных смесей несовместимых полимеров (ПЭВД, ПС, ПВХ), общая поверхность раздела фаз ещё больше, а отсутствие адгезии между этими фазами приводит к тому, что физико-механические свойства этих смесей намного соответствующих характеристик исходных высокомолекулярных соединений.

Основные физико-механические свойства двойных и тройных смесей из ПЭВД, ПС и ПВХ, соединяющих 10, 20 и 30% СЭВА, представлены в таблице 2.

Из анализа данных таблицы 2 видно, что при смешивании ПЭВД, ПС и ПВХ с СЭВА наблюдается уменьшение прочности при растяжении и удлинение при разрыве для полимера с добавкой СЭВА. Для смесей ПВХ—СЭВА и ПС—СЭВА наблюдается резкое падение прочности при растяжении, тогда как для смесей ПЭВД—СЭВА уменьшение этой характеристики носит гораздо менее резкий характер. Для смеси ПЭВД—СЭВА наблюдается сперва лёгкое падение удлинения при разрыве, с последующим ростом этой характеристики при дальнейшем увеличении содержания СЭВА в системе.

Рассматривая изменение ударопрочности по Изоду для смесей, состоящих из полимера (ПЭВД, ПС или ПВХ) и СЭВА, с изменением содержания СЭВА, можно отметить следующее : для системы ПВХ—СЭВА наблюдается максимум характеристики при 20%-ом содержании СЭВА; для системы ПЭВД—СЭВА наблюдается непрерывное уменьшение харак-

Таблица 2

Состав и свойства смесей ПЭВД, ПС и ПВХ с добавкой СЭВА

Пор. но. испытания	Состав смесей, [%]				Свойства смесей		
	ПЭВД	ПС	ПВХ	СЭВА	Прочность при растяжении кгс/мм²	Удлинение при разрыве %	Ударопрочность по Изоду кгс. см/см
11	90	—	—	10	0,95	455	41,0
12	80	—	—	20	0,84	465	30,0
13	70	—	—	30	0,61	505	26,5
14	60	30	—	10	0,805	10,0	14,0
15	53,3	26,7	—	20	0,35	35,0	30,0
16	46,7	23,3	—	30	0,135	100	8,75
17	30	60	—	10	1,375	1,8	3,5
18	26,7	53,3	—	20	0,925	7,7	3,8
19	23,3	46,7	—	30	0,375	19,5	10,5
20	—	90	—	10	1,80	1,0	4,0
21	—	80	—	20	1,05	3,1	6,3
22	—	70	—	30	0,495	6,0	8,5
23	—	60	30	10	2,125	1,0	1,65
24	—	53,3	26,7	20	2,25	3,5	5,0
25	—	46,7	23,3	30	1,0	8,0	6,7
26	—	30	60	10	2,075	4,0	2,3
27	—	26,7	53,3	20	0,45	4,5	5,3
28	—	23,3	46,7	30	0,125	12,0	12,1
29	—	—	90	10	3,1	18,0	17,0
30	—	—	80	20	0,7	16,5	29,5
31	—	—	70	30	0,4	24,0	22,0
32	30	—	60	10	0,80	2,0	3,2
33	26,7	—	53,3	20	0,35	9,5	13,1
34	23,3	—	46,7	30	0,075	25,0	19,4
35	60	—	30	10	0,5	12,0	7,0
36	53,3	—	26,7	20	0,235	16,5	26,0
37	46,7	—	23,3	30	0,1	54,5	31,0
38	30	30	30	10	0,825	0,1	1,3
39	26,7	26,7	26,6	20	0,375	0,1	2,2
40	23,3	23,3	23,4	30	0,05	0,1	11,3

теристики с ростом содержания СЭВА ; в случае же смеси ПЭ—СЭВА, наблюдается рост характеристики с увеличением содержания СЭВА.

При сравнительном анализе влияния добавки СЭВА на смеси двух полимеров (ПЭВД—ПС, ПЭВД—ПВХ и ПС—ПВХ), можно установить, что прочность при растяжении для смесей ПЭВД—ПС и ПС—ПВХ достигает максимума при добавке 10% СЭВА, а в случае системы ПЭВД—ПВХ наблюдается непрерывное уменьшение этой характеристики с увеличением содержания СЭВА в смеси, независимо от соотношения основных полимеров (рис. 1).

Для всех исследованных двойных смесей, удлинение при разрыве увеличивается с увеличением содержания СЭВА в системе (рис. 2).

Ударопрочность по Изоду для двойных смесей, содержащих, помимо основных полимеров, добавку СЭВА, зависит от соотношения основных полимеров (рис. 3). Для смесей с соотношением ПЭВД/ПС, ПЭВД/ПВХ и ПС/ПВХ равным 1/2 (рис. 3 *А*), введение СЭВА приводит к увеличению

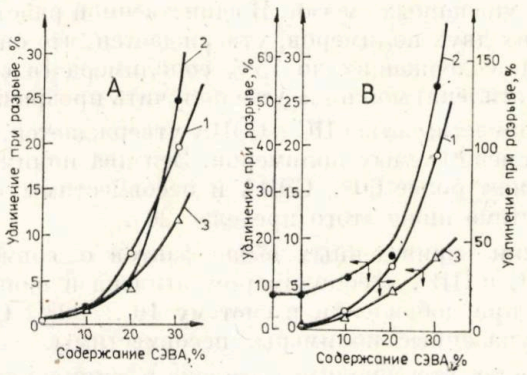


Рис. 1. — Изменение прочности при растяжении образцов из смесей ПЭВД—ПС (*1*), ПЭВД—ПВХ (*2*) и ПС—ПВХ (*3*) с изменением содержания СЭВА в системе; соотношение основных полимеров в смеси: *A*—1/2; *B*—2/1.

ударопрочности по Изоду в случае ПЭВД—ПВХ и ПС—ПВХ, а в случае системы ПЭВД—ПС эта характеристика проходит через минимум, соответствующий добавке 10% СЭВА.

Изменение соотношения смешиваемых основных компонентов в вышеуказанных двойных систем (2: 1 вместо 1: 2—рис. 3 *B*) ведёт к изменению вида зависимости ударопрочности по Изоду от содержания СЭВА в системе. В этом случае, для смесей ПЭВД—ПВХ и ПС—ПВХ наблюдается минимум ударопрочности при 10%-ом содержании СЭВА, а для системы ПЭВД—ПС эта характеристика проходит через максимум при 20%-ом содержании СЭВА в системе.

Для того, чтобы объяснить влияние добавок СЭВА на двойные и тройные смеси на основе ПЭВД, ПС и ПВХ, следует расмотреть совместимость этого сополимера с каждым из указанных полимеров.

Исследования, проведённые для изучения совместимости ПВХ и сополимеров этилена и винилацетата показали, что совместимость этих высокомолекулярных соединений зависит от содержания винилацетата в сополимере [13] ... [16]. Только сополимеры с содержанием ВА более 50% совместимы с ПВХ [13], [15].

Из этого следует, что использованный нами сополимер этилена и винилацетата, с содержанием ВА 45%, несовместим с ПВХ и, вследствие этого, смеси, образуемые этими двумя высокомолекулярными соединениями будут гетерогенными. Это предположение подтверждается экспериментальными данными (таблица 2) ; из этих данных следует, что введение СЭВА и ПВХ приводит к уменьшению прочности при растяжении для этого полимера, одновременно с увеличением удлинения при разрыве ; такое поведение характерно для несовместимых полимеров. Наибольшее значение характеристики, соответствующее смеси с добавкой 20% СЭВА, объясняется тем, что при таком составе смеси осуществляется оптимальное диспергирование частиц сополимера в жёсткой матрице из ПВХ.

В литературе мало данных о смесях из ПЭВД и СЭВА. Эти данные представлены реологическими [11], [18] и физико-механическими харак-

теристиками [18] указанных смесей. В единственной работе, обсуждающей совместимость этих двух полимеров, утверждается, что они несовместимы, но что из смесей, содержащих до 75% сополимера (в составе которого входит 80 мол % этилена) можно все же получить прозрачные плёнки [19].

В связи с совместимостью ПС с СЭВА утверждается, что она зависит от соотношения смешиваемых полимеров. Эти два полимера совместимы, если смесь содержит более 60% СЭВА и несовместимы если содержание сополимера в системе ниже этого предела [20].

На основании приведенных выше фактов о совместимости полимеров ПЭВД, ПС и ПВХ с сополимером этилена и винилацетата можно утверждать, что при добавлении в систему 10 ... 30% СЭВА, смеси, содержащие вышеуказанные полимеры, несовместимы.

Несмотря на то, что сополимер этилена и винилацетата несовместим с основными полимерами смеси, при содержании в сополимере 45% ВА, наблюдается некоторое улучшение физико-механических свойств при добавлении такого сополимера, что объясняется адгезионным эффектом групп винилацетата в сополимере [21] ... [23]. Присутствие СЭВА в исследованных смесях способствует росту межфазной-адгезии в системе и обеспечивает более тонкое диспергирование фаз. Результатом такого эффекта является увеличение удлинения при разрыве и рост ударопрочности по Изоду для смесей, содержащих СЭВА ; это увеличение тем существенее, чем выше содержание сополимера в системе. Оптимальные соотношения СЭВА, при использовании последнего в качестве агента для улучшения совместимости исследованных смесей, колеблются в пределах 10 ... 20%.

4. Выводы

Проведённые исследования по использованию сополимера этилена и винилацетата (содержащего 45% ВА) в качестве агента для улучшения совместимости двойных и тройных смесей на основе ПЭВД, ПС и ПВХ дали возможность установить следующее :

а) физико-механические свойства двойных и тройных смесей на основе ПЭВД, ПС и ПВХ намного ниже физико-механических свойств исходных полимеров, что объясняется их несовместимостью ;

б) добавление 10 ... 30% СЭВА приводит к улучшению ударопрочности по Изоду и удлинения при разрыве для смесей, составленных из вышеуказанных основных полимеров, но вместе с тем эта добавка ведёт к ухудшению при растяжении ; исключением от этого правила являются смеси ПЭВД—ПС и ПС—ПВХ, для которых кривые, изображающие изменение прочности при растяжении при изменении содержания СЭВА в системе, проходят через максимум, который соответствует добавке 10% агента по улучшению совместимости ;

в) сополимер этилена и винилацетата (с содержанием 45% ВА) может быть использован в качестве агента совместимости для двойных и тройных смесей на основе компонентов ПЭВД, ПС и ПВХ. Эффект совместимости, получаемый при введении этого сополимера, объясняется присутствием в СЭВА групп ацетата, вызывающих, благодаря их адге-

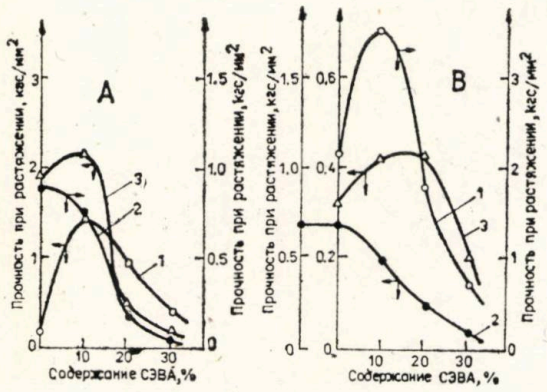


Рис. 2. — Изменение удлинения при разрыве для образцов из смесей ПЭВД—ПС (*1*), ПЭВД—ПВХ (*2*) и ПС—ПВХ (*3*) в зависимости от содержания СЭВА в системе; соотношение основных полимеров в смеси : *A* — 1/2 ; *B* — 2/1.

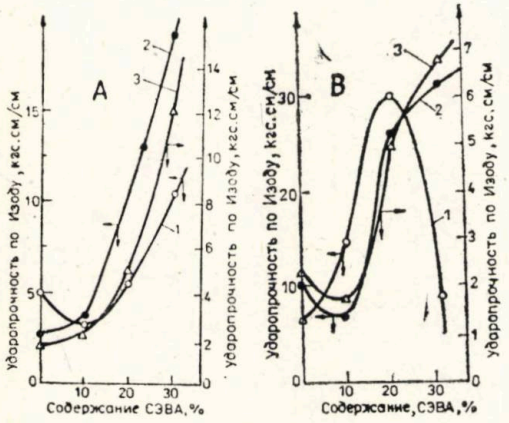


Рис. 3. — Изменение ударопрочности по Изоду для смесей ПЭВД—ПС (*1*), ПЭВД—ПВХ (*2*) и ПС—ПВХ (*3*) с содержанием СЭВА в системе ; соотношение основных полимеров в смеси : *A* — 1/2 ; *B* — 2/1.

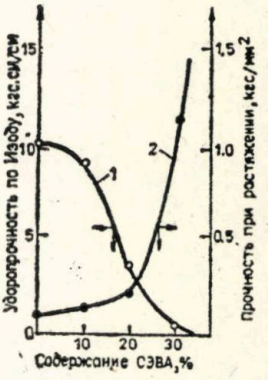
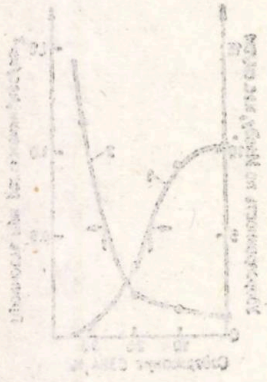
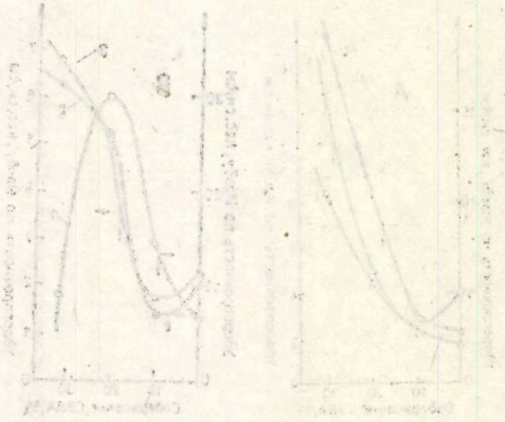


Рис. 4. — Изменение прочности при растяжении (*1*) и ударопрочности по Изоду (*2*) с содержанием СЭВА, для тройной смеси, состоящей из равных частей ПЭВД, ПС и ПВХ.

B
A





зионному характеру, улучшение межфазной адгезии в системе и способствующих лучшему диспергированию фаз.

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AMESTECURI DE POLIMERI

I. Proprietăți fizico-mecanice

(Rezumat)

S-a studiat influența adaosului de copolimer etilenă—acetat de vinil (EVA) în amestecurile binare și ternare din polietilenă, polistiren și policlorură de vinil, în vederea stabilirii faptului dacă acest compus poate fi utilizat drept agent de compatibilizare pentru sistemele menționate. Acțiunea de compatibilizare observată constituie rezultatul prezenței în copolimerul EVA a grupelor acetat, care, datorită caracterului lor adeziv, îmbunătățesc adeziunea dintre fazele sistemului și realizează o mai bună omogenizare a amestecului.

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DEGRADATION FILMS OF ABS–POLYETHYLENE MIXTURES

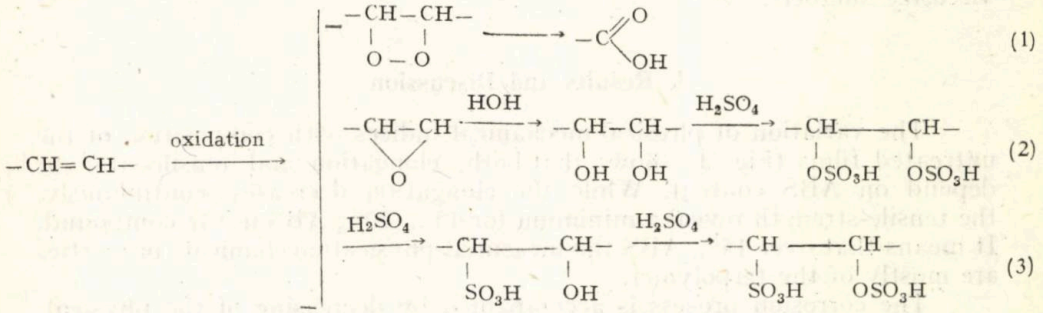
I. HYDROLYTIC-OXIDATIVE DEGRADATION

BY

M. NICU, VIORICA NICU and ROMULUS-ION FILIP

1. Introduction

ABS is one of the few polymers used to obtain metallized objects [1]...[5]. It was found that metallizing process is mainly influenced by the corrosion technology, and it was studied with regard to chemical nature and working parameters of the activation bath. Less studied are chemical and physical modifications occuring in the polymer, also their implications on physical-mechanical properties of final products. Various investigators have reached different conclusions regarding chemical modifications in the polymer microstructure. Some of them consider that butadiene units are the support for some oxidation reactions followed by esterification and decarboxylation [1]...[3] which should be case evidenced by IR spectroscopy; other authors [5] showed hat IR spectra of the corroded ABS do not differ from those of the initial polymer. Recently, the utility of IR investigation of the corrosion process was once more proved [6].



Our studies refers to the modifications in microstructure and physical-mechanical properties of the films from ABS – polyethylene compounds.

2. Experimental

Films of 0.05 mm thickness were prepared from the mixtures listed in Table 1 using a POLYMEX-90 type extruder.

By optical microscopy the homogenity of the ABS–polyethylene mixtures was found to be good.

Samples of these films were treated at 61°C in a corrosion bath with the following composition :

a) chromic anhydride . . . . . 355 g,

b) sulphuric acid (d =1.83 kg/l) · · · · · · · · 444 g,
c) water · 682 g.

Table 1

Composition of the ABS—Polyethylene Compounds (% by weight)

ABS	0	5	10	15	20	25
Polyethylene	100	95	90	85	80	75
Symbol	1	2	3	4	5	6

The corrosion times were 5 ; 10 ; 15 ; 20 ; 25 ; 30 ; 35 and 40 min. Subsequently the films were washed and dried.

The stress — strain curves were registered on an INSTROM apparatus taking the mean values from five measurements. From the offered data by stress — strain curves, the tensile strength (N/m^2) and stretching were computed for all types of mixtures and all corrosion times.

The IR spectra were registered on a SPECORD apparatus.

Viscosity measurements were performed in *p*-xilene solution. They showed that the degradation process is accompanied by lowering of the viscosity numbers.

3. Results and Discussion

The variation of physical-mechanical indices with composition of the untreated films (Fig. 1) shows that both, elongation and tensile-strenght depend on ABS content. While the elongation decreases continuously, the tensile-strength reveal a minimum for 15 ... 20% ABS in the compound. It means that over 15% ABS the measured physical-mechanical properties are mostly of the terpolymer.

The corrosion process is accompanied by decreasing of the physical-mechanical indices (Figs. 2 and 3) ; degradation process is more pronounced at larger times.

As it was expected, from the dependence of physical-mechanical properties on composition (Fig. 4), results that main degradative process occurs in ABS component.

Simultaneously decreasing of tensile-strength and elongation suggests that the degradation process goes along with lowering of the molecular weight and intermolecular forces.

To certify this conclusion and to follow microstructural transformations in polymers during corrosion process, were used the IR spectra registered for the corroded samples. The comparative analysis of these data (Fig. 5) show some structural changes mostly in three regions, namely :

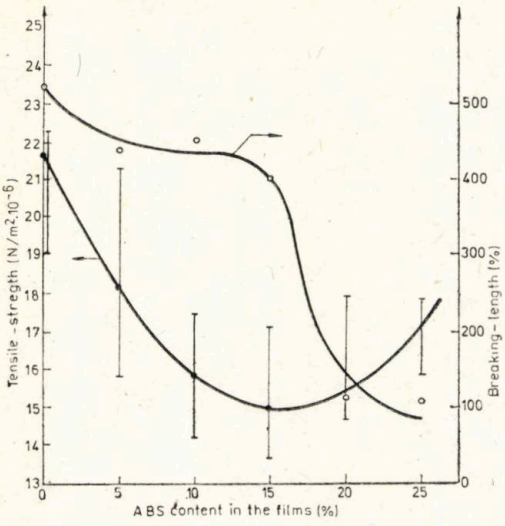


Fig. 1. — Dependence of tensile-strength and breaking-length on ABS content in the films.

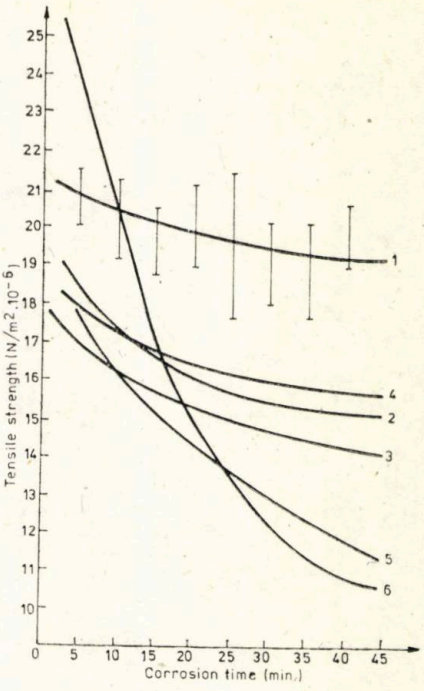


Fig. 2. — The influence of corrosion time on tensile-strength.

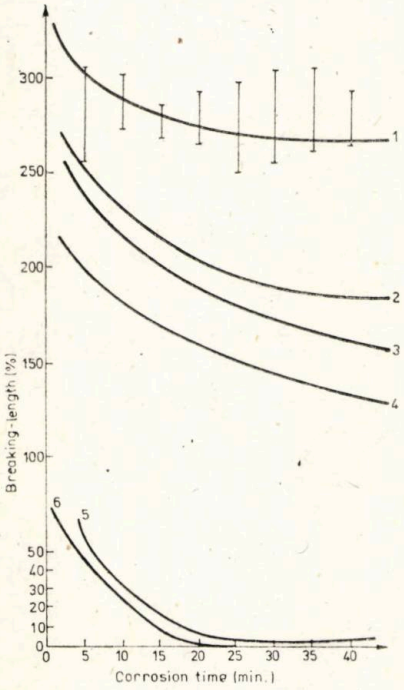


Fig. 3. — The influence of time on breaking-length.

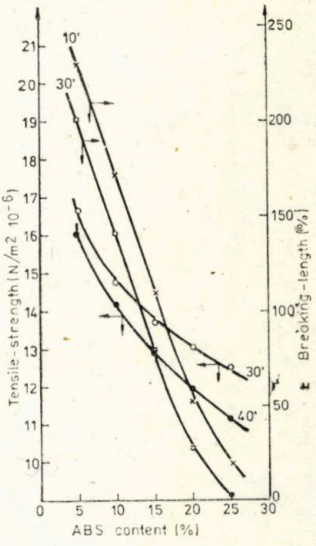
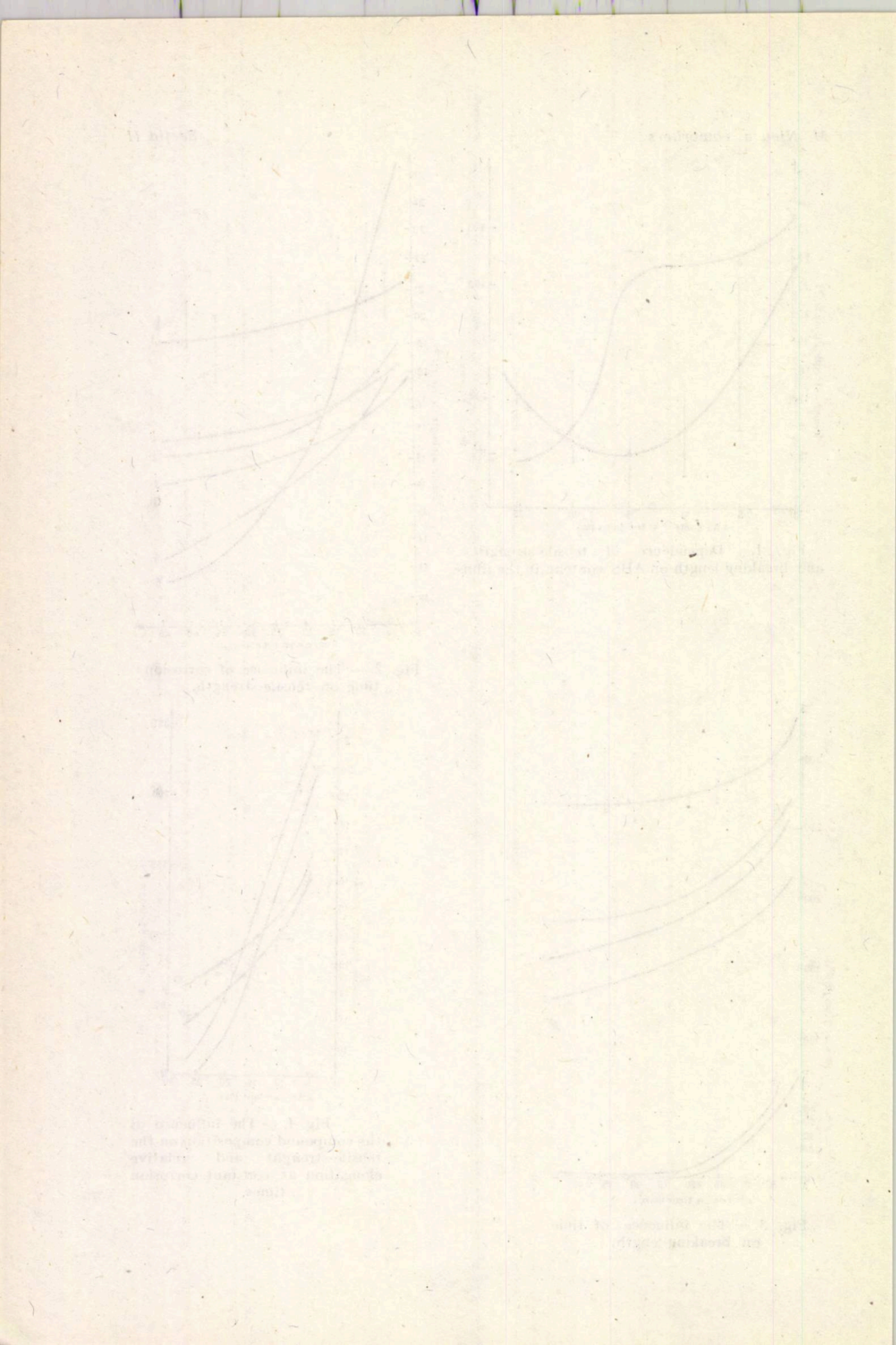


Fig. 4. — The influence of the compound composition on the tensile-strenght and relative elongation at constant corrosion times.



900 ... 1 000 cm^{-1} (vinyl groups), 1 500 ... 1 750 cm^{-1} (amidic, carboxylic and vinylic groups) and 2 240 cm^{-1} (nitrile groups) [8].

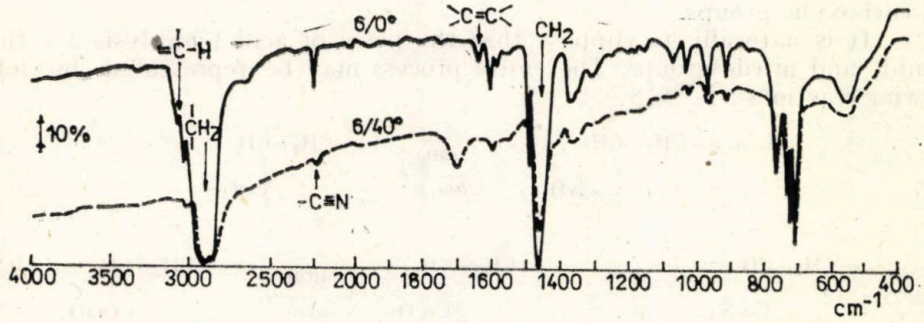


Fig. 5 — The IR spectra of the undergradated films containing 25% ABS (6/0°) reference and corroded 40 min. (6/40°).

Since the reference spectra (6%) show amidic groups it shoud be considered that the ABS contained in the mixture, realy is a quaternar copolymer (AN+B+S+AM). The acrylamide (AM) units (identified also in ABS spectra) appear during the synthesis and processing. In the former case they result from hydrolysis of nitril groups, in the last one hydrolysis occurs due the absorbed water by ABS and high processing temperatures. Both, the IR spectra and the physical-mechanical data place the chemical modifications mainly in the ABS units (Fig. 6), the extent of degradation depending on corrosion time (Fig. 7).

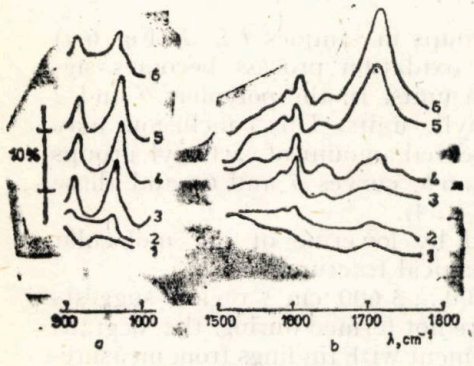


Fig. 6. — Signal intensities for various ABS content at constant corrosion time (30 min.) : *a* — zone 900...1 000 cm^{-1} ; *b* — zone 1 500...1 800 cm^{-1}.

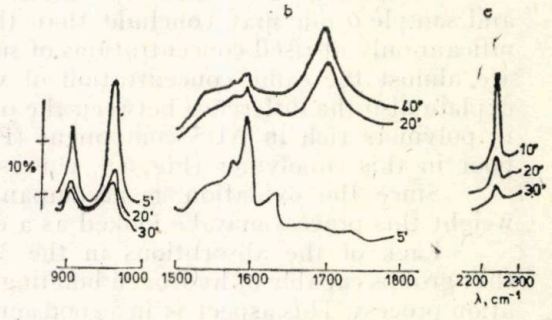
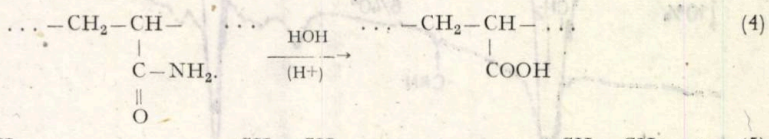


Fig. 7. — The IR spectra of the degradated films containing maximum amount of ABS (25%) : *a* — 900...1 000 cm^{-1} ; *b* — 1 500... 1 800 cm^{-1} ; *c* — 2 240 cm^{-1}.

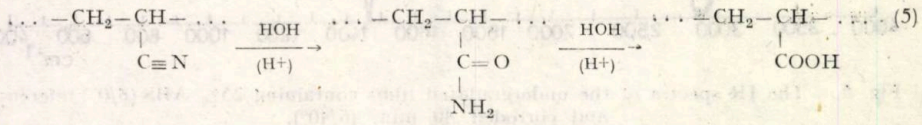
Spectral data (Fig. 7) show some structural modifications which occur during chemical corrosion and they consist in lowering of amidic (*b*), nitrilic (*c*) and vinylic (*a* and *b*) concentration at the same time with increasing of the carboxylic ones (*b*). These facts toghether with the composition

of the corrosion bats assert that the chemical degradation is a result of superpasing of hydrolytic and oxidation processes which affect mainly the amidic, nitrilic and vinylic groups, having as the final result formation of carboxylic groups.

It is naturally to suppose that the place of acid hydrolysis are the amide and nitrile groups. The entire process may be represented by following reactions :



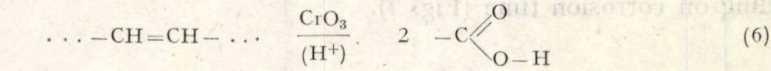
(4)



(5)

Since the content of amidic and carboxylic groups lowers (s. IR spectra), the hydrolysis rate of amidic groups should be higher than of the nitrilic ones. In the contrary case an increasing of the amidic groups should be observed.

Data presented in Fig. 6 *b* show that the concentration of amidic groups in samples *3* ... *6* are almost constant but the content of carboxylic ones increases. This may suggests that the last groups forms both, by hydrolysis and by oxidation of vinylic units in presence of CrO_3 and H_2SO_4 following the reaction :



(6)

Comparing the content of vinylic groups in samples *1* ... *3* (Fig. 6 *a*) and sample *6* one may conclude that the oxidation process becomes significant only at rised concentrations of such units. In the polymers *6* and *2* are almost the same concentration of vinylic units. This conclusion may explain also the difference between the observed amount of carboxyl groups in polymers rich in ABS component (Fig. 6 *b*, curves *5* and *6*) and those poor in this copolymer (Fig. 6 *b*, curves *1* ... 4).

Since the oxidation is accompanied by lowering of the molecular weight this process may be looked as a chemical fracture.

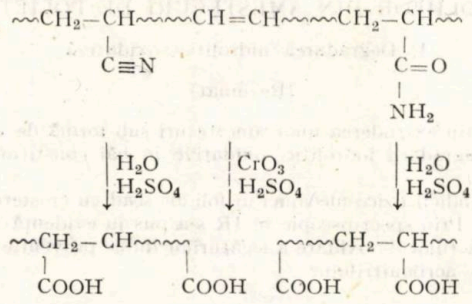
Lack of the absorbtions in the 3 300 ... 3 600 cm^{-1} region suggests that groups capable of hydrogen bonding are not formed during the degradation process. This aspect is in a good agreement with findings from measurements of physical-mechanical indices and it also assert that the carboxyl groups formed during oxydation are not so numerous.

The polyethylene — as main polymer in compounds — modifies during the corrosion process only by oxidation leading in some extent to carboxyl groups (Fig. 6 *b*, curve *1*).

As it was already mentioned [3] the corrosion process may be explained also through the formation of sulphonic and sulphonates derivatives [2], [3], but this point of vue was not generally accepted [6].

In our investigations we did not find any absorbtion in the 1 000 ... 1 200 cm^{-1} region (characteristic for SO_2) so it is difficult to believe the formation of sulphonic derivatives. Particularly we worked in diluted H_2SO_4 and it is known that these conditions are not propre to form sulphonic esters [7].

To resume the conclusions drown from the IR spectroscopy the following scheme may be presented :



4. Conclusions

In order to investigate degradation process of ABS and polyethylene compounds from these materials were extruded pelicules which were submitted to chemical corrosion and physical-mechanical indices were measured.

The obtained data led to the following conclusions :

1. Up to 15% ABS in the compound, the materials reveal mostly properties of the polyethylene : for higher content will dominate the ABS characteristics.

2. During chemical corrosion the physical-mechanical indices of the compounds decrease.

3. Chemically the corrosion is a hydrolytic-oxidative process. It is accompanied by hydrolytic degradation of nitril and amidic groups also by scision of macromolecular chain due to the oxidation of vinylic units.

4. At constant temperature the chemical and physical-mechanical modifications depend on ABS content and corrosion time.

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DEGRADAREA FOLIILOR DIN AMESTECURI DE POLIETILENĂ CU ABS

I. Degradarea hidrolitico-oxidativă

(Rezumat)

Foliile obținute prin extruderea unor amestecuri sub formă de granule de polietilenă și ABS au fost supuse degradării hidrolitico-oxidative în băi constituite din $CrO_3 + H_2SO_4 +$ $+ HOH$ la 61°C.

S-a constatat că indicii fizico-mecanici ai foliilor scad cu creșterea conținutului de ABS și a timpului de reacție. Prin spectroscopie în IR s-a pus în evidență faptul că degradarea se datorește în principal reacțiilor de oxidare a legăturilor duble provenite din butadienă și hidrolizei grupelor nitril ale acrilonitrilului.

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SPECTRAL STUDY OF REACTIVITY OF SOME ARYL DIAZONIUM CATIONS

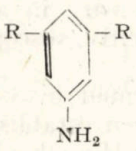
BY

VALERIA GORDUZA, N. FOCA, I. COCÂRLĂ and VIANORA PEŞCARU

1. Introduction

Brodening the asortments of azoic dyes and pigments with compatible products with hydrophobic materials and higher tinctorial properties calls for the study of reactivity of some aryl diazonium cations substituted in aromatic ring with the electron-withdrawing groups such as nitro, amido, ester, nitryl a.s.o.

In this context, reactivity of some amines (I) and cations of the form (II) have been investigated :

(I *a*, *b*)  (II *a*, *b*)

where R = —COOH (*a*), —$COOCH_3$ (*b*), the latter being applied in synthesis of aceto-acetyl-amino-benzimidazolone azo-pigments [1].

The performed studies by correlation of the spectral data with structural parameters given by molecular diagrames focused the kinetics of the aryl diazonium cations (II) reactions in aqueous medium at different pH and temperature as well as in the presence of a substrate with high nucleophilicity. Under these conditions, in the aqueous solutions are possible the acid — base tautomerism and stereochemical equilibria as well as nucleophilic or electrophilic substitution reactions, depending on the role of the aryl diazonium cation, substrate against nucleophilic reactant or reactant against activated aromatic substrates and compounds with reactive methylene groups, as shown by reaction diagram (1).

The aryl-diazonium cations (II *a*, *b*) have been obtained by classical method of diazotization with $NaNO_2$, in dilute mineral acid medium, according to the reactions scheme (2).

2. Experimental

Diazotization of 5-amino-isophthalic acid and 5-amino-dimethyl-isophtalate was carried out in the presence of 5N HCl, at a molar ratio amine to acid mineral of 1 : 3 with 5N $NaNO_2$ in stoichiometric ratio.

The acid — base tautomerism and stereochemical equilibrium have been performed by dilution of a little volume solution of aryl diazonium salt with a volume of 10^2 times larger solution with adequate pH. The solution of 0.1 M borate and phosphate have been employed as buffer and *m*-nitrophenol ($pK_a = 8.25$) as indicator. Thermal decomposition, in aqueous medium, of the aryl-diazonium cation was carried out in the temperature range of 35° ... 65°C.

In electrophilic reactivity of aryl-diazonium cation has been appreciated on the basis of β-naphthol test, using the stoichiometric coupling ratio, pH = 8 and concentrations of $(2.5 \ldots 10) \times 10^{-5}$ M.

All measurements have been performed spectrophotometrically, using 1 cm quartz cell on a spectrophotometer Specord UV—VIS, Carl Zeiss, Jena.

Concentrations of the products and intermediates of the studied reactions have been determined by means of the calibration curves, absorbancy — concentration, in the range of Lambert-Beer's law respect.

3. Results and Discussion

3.1. Study of the Reactivity on the Basis of HMO Calculations

Study of the electronical density distribution in the amines of type (I) is two fold important, namely :

a) mode in which the electron-attracting substitutes in mutual position *meta* diminishing the electronic density in aromatic ring can affect basicity of aminic nitrogen and, implicitly, susceptibility to diazotization reaction ;

b) reactivity of diazoderivate formed by coupling reaction.

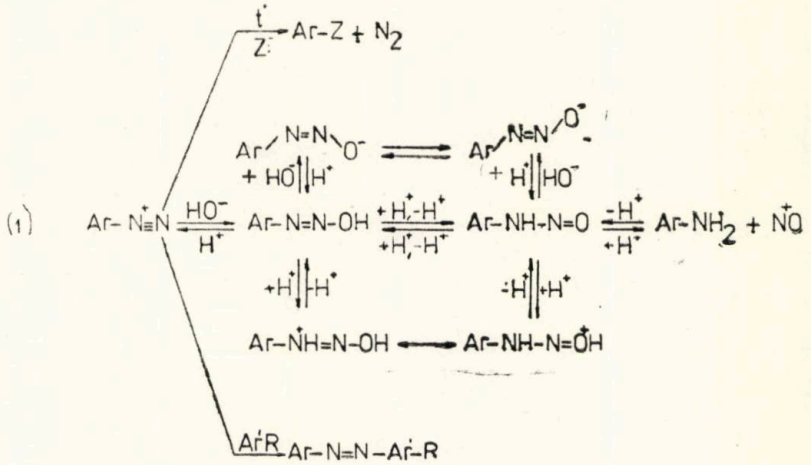
The molecular diagrames have been established based on application of the method of molecular orbitals with Hückel's approximation (HMO) and the parameters employed, adopted according to Steitwieser [2], are summarized in Table 1.

Table 1

The HMO Parameters [2]

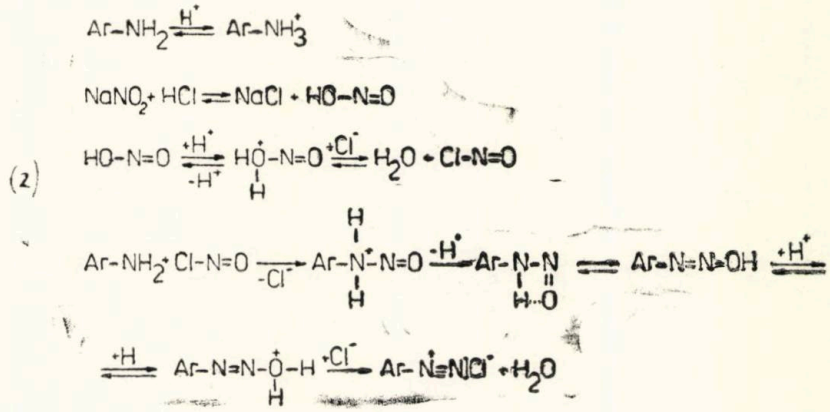
Group	h_x	Bond	K_{y-x}
$-NH_2$	1.5	$Ar-NH_2$	0.8
$(-N\equiv)$ or $(\equiv N)$	1.25	$-N=N-$	1
$-OH$	2	$Ar-OH$	0.8
$-\dot{O}$ (carbonyl)	1.2	$C=O$	1.1
$\dot{C}$ (carbonyl)	0.2	$C-O$	0.9

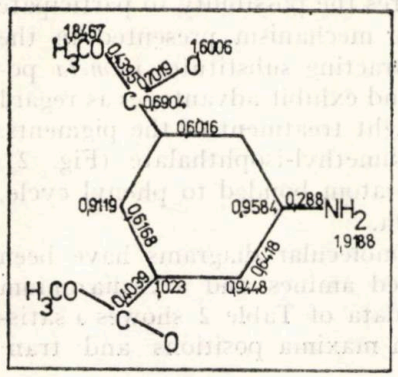
The molecular diagrams of 5-amino-dimethyl-isophthalate and 5-amino-isophthalic acid (Fig. 1), show distributions of the electronic densities similar in the two structures and ensuring a nucleophilicity relative



$Z^- = {}^-OH, {}^-Cl, {}^-Br, {}^-CN$

$R = OH, -NH_2$





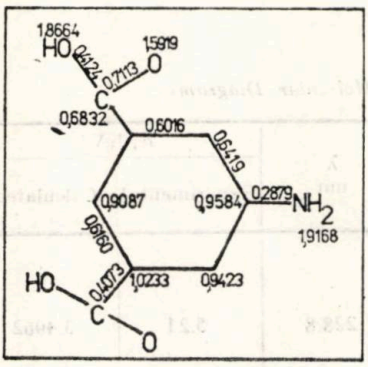


Fig. 1. — Molecular diagrams of 5-amino-dimethyl-isophthalate and 5-amino-isophthalic acid.

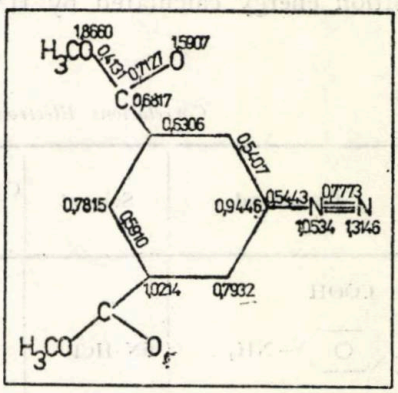


Fig. 2. — Molecular diagram of the aryl diazonium cation (II *b*).

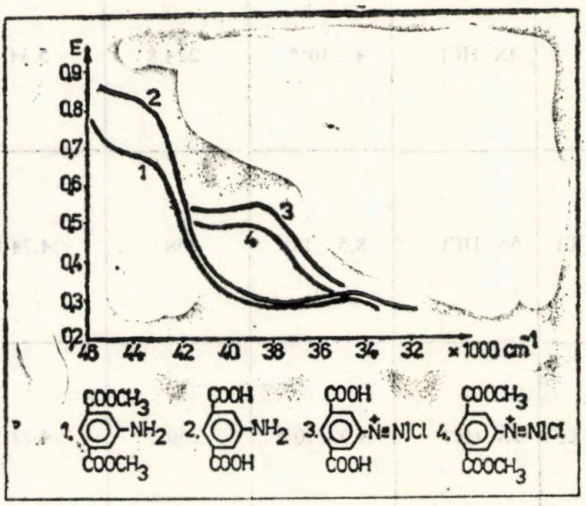


Fig. 3. — Absorption spectra of the amines and aryl-diazonium cations studied.

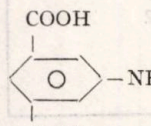
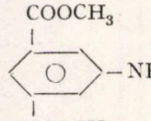
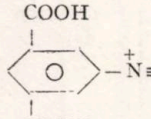
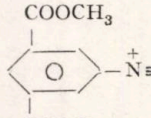
high at the aminic nitrogen atom, that ensures the possibility to participate at diazotization reaction, according to the mechanism presented in the reactions scheme (2). Thus, the electron-attracting substitutes in *meta* position affect only a little basicity of amine and exhibit advantages as regard the resistance improving against wet and light treatment of the pigments.

The molecular diagram of 5-amino-dimethyl-isophthalate (Fig. 2), points out a deficit of electrons at nitrogen atom bonded to phenyl cycle, fact in good agreement with literature data.

On the other hand, the features of molecular diagrams have been correlated with electronic spectra of studied amines and aryl-diazonium cations formed (Fig. 3 and Table 2). The data of Table 2 showes a satisfactory correlation between the absorption maxima positions and transition energy calculated by HMO method.

Table 2

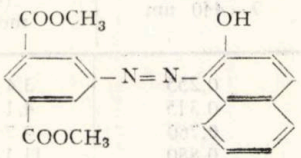
Correlations Electronical Spectra—Molecular Diagrams

Compound	Solvent	Concentration mol. l^{-1}	λ nm	E, [eV]	
				Experimental	Calculated
	5N HCl	6.7×10^{-6}	228.8	5.21	3.4962
	5N HCl	4×10^{-6}	224.8	5.34	3.5226
	5N HCl	8.5×10^{-6}	258	4.74	—
	5N HCl	4.9×10^{-6}	259.5	4.72	3.9093

3.2. Electrophilic Reactivity of the Aryl-diazonium Cation Investigated

Behaviour of the aryl-diazonium cation (II *b*) in the coupling reaction with β-naphthol to form the dye with the structure (III), has been studied:

(III)



Absorption spectrum of the compound (III), presented in Fig. 4, recorded in solution of 2% NaOH, at concentration of 1.10^{-4} M, exhibits two absorption maxima at 342 nm ($\varepsilon = 7\,600$ l mol^{-1} cm^{-1}) and 440 nm ($\varepsilon = 9\,200$ l mol^{-1} cm^{-1}).

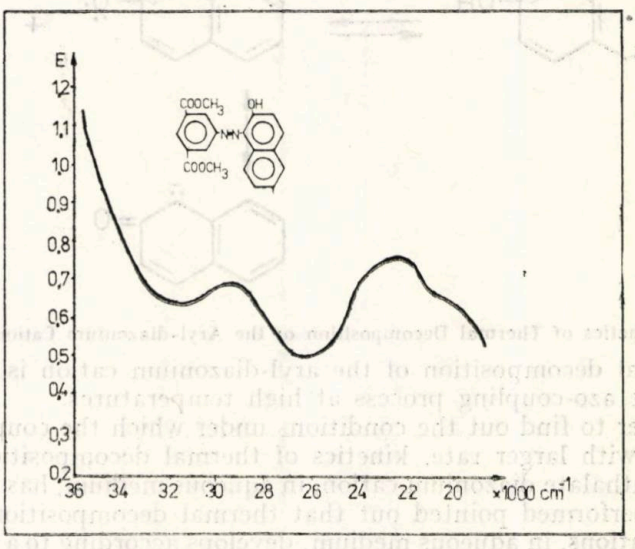


Fig. 4. — Absorption spectrum of compound (III).

Spectrophotometrical measurements of the content of diazoderivat at different instant of diazotization reaction have been carried out by correlation of absorption with calibration curve, absorbancy—concentration, for compound (III) in the concentration range of $(1 \ldots 10) \times 10^{-5}$ mol l^{-1} and pH = 7 ... 9.

Results of the spectrophotometrical measurement are presented in Table 3. There is a maximum of the aryl diazonium cation (II *b*) concentration after 40 min. of diazotation, followed by its decomposition or inactivation due to the possible acid — base equilibriums.

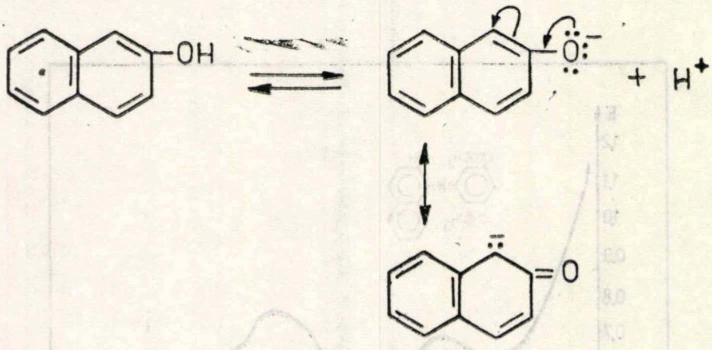
Reactivity of the aryl-diazonium cation (II *b*) in reaction with β-naphtol is maximum if pH = 8, fact explainable taking into account the activation preequilibrium of β-naphthole:

Table 3

Reactivity of the Aryl-diazonium Cation (II b) in Azocoupling with β-naphthol

Sample	Diazotization time, min.	Absorbancy at $\lambda = 440$ nm	Concentration of (III) mol. l^{-1}	Concentration of (II *b*) mol. l^{-1}
1	10	0.255	3.4×10^{-5}	2.5×10^{-5}
2	20	0.315	4.1×10^{-5}	3.02×10^{-5}
3	30	0.760	9.7×10^{-5}	7.15×10^{-5}
4	40	0.880	11.1×10^{-5}	8.18×10^{-5}
5	50	0.360	4.7×10^{-5}	3.46×10^{-5}
6	60	0.285	3.7×10^{-5}	2.73×10^{-5}

Data of Table 3 have been obtained at $t = 15°C$ and pH= 8.



(IV)

3.3. Kinetics of Thermal Decomposition of the Aryl-diazonium Cation (II *b*)

Thermal decomposition of the aryl-diazonium cation is a controlling factor of the azo-coupling process at high temperatures.

In order to find out the conditions under which the coupling reaction takes place with larger rate, kinetics of thermal decomposition of the dimethyl isophthalate diazonium cation, in aqueous medium, has been studied. The study performed pointed out that thermal decomposition of the aryl diazonium cations, in aqueous medium, develops according to a SN1 mechanism, having as controlling rate step heterolysis of substrate.

$$Ar-\overset{+}{N}\equiv N \xrightarrow{\text{slowly}} Ar^{+} + N_2$$

(V)
$$Ar^{+} + H_2O \xrightarrow{\text{fast}} Ar-\underset{\underset{H}{|}}{\overset{+}{O}}-H \rightarrow Ar-OH + H^{+}$$

During the latter step, a rapid one, the phenyl carbonium ion, occured by monomolecular dissociation of the C—N bond, is attacked by water, as nucleophilic agent, with nitrogen releasing and phenol formation.

In the aqueous neutral or weak alkaline medium, kinetics of the aryl-diazonium cation (II *b*) decomposition is of the first order

(VI)
$$-\frac{d[ArN_2^+]}{dt} = k_1[ArN_2^+].$$

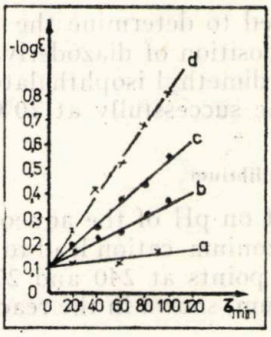


Fig. 5. — Dependence of absorbancy on time.

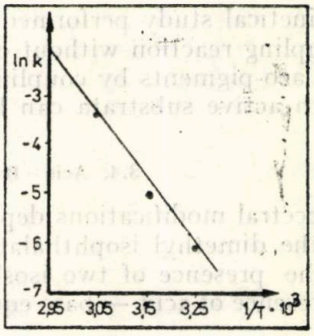


Fig. 6. — Arrhenius's plot.

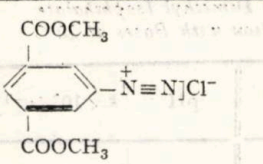
Mareover, these results agree with the kinetical data of cited literature [4], [5].

The decomposition rate of dimethyl isophthalate diazonium cation was determined based on absorbancy variation at 260 nm. The kinetical parameters have been determined graphically, using the diagram absorbancy vs. time (Fig. 5). The values of the reaction rate constant are presented in Table 4.

The activation energy and preexponential factor have been estimated based on dependence $\ln k = f(1/T)$ plotted in Fig. 6, according with Arrhenius's law.

Table 4

Reaction Rate Constant of the Dimethyl Isophthalate Diazonium Cation Decomposition

Compound	Temperature, [°K]	k, [s^{-1}]
	308	0.0024
	318	0.0108
	328	0.0299
	338	0.0528

Thus,

(VII) $$k = Ae^{-E_a/RT},$$

or in logarithmic form

(VIII) $$\ln k = \ln A - \frac{E_a}{RT}.$$

The activation energy was 22.362 KJ.mol^{-1}, and preexponential factor was 4.798×10^9 s^{-1}.

The kinetical study performed allowed to determine the temperature range of coupling reaction without decomposition of diazoderivative. Thus, synthesis of azo-pigments by coupling the dimethyl isophthalate diazonium chloride with active substrata can be done successfully at 20°C.

3.4. Acid – Base Equilibrium

The spectral modifications dependent on pH of the aqueous solutions containing the dimethyl isophthalate diazonium cation lead to curves families and the presence of two isosbestic points at 240 and 276 nm, that prove the presence of acid — base equilibrium, shown in the reaction scheme (1).

The spectral characteristics of the species involved in these acid — base equilibriums are listed in Table 5.

Table 5

Spectral Characteristics of the Aryl-diazonium Cation and the Species Involved in Acid – Base Equilibrium

Compound	λ, [nm]	log λ
$Ar-\overset{+}{N}\equiv N$	260	4.16
$Ar-N=N-OH$	310	3.40
cis $Ar-N=N-O^-$	300	3.83
trans $Ar-N=N-O^-$	340	4.15
isosbestic points	240	
	276	

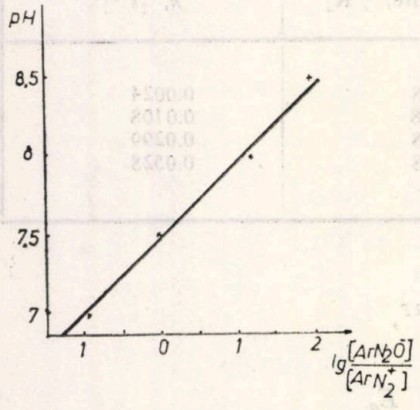


Fig. 7. — Dependence of pH on the ratio ArN_2O^-/ArN_2^+.

Table 6

Reaction of the Dimethyl Isophthalate Diazonium Cation with Bases at 20°C

pH	$k \times 10^2$, [s^{-1}]	pH	$k \times 10^2$, [s^{-1}]
7	0.023	10	2.64
8	0.1	11	2.98
9	1	12	3.01
		14	3.09

The plot of pH vs. log (ArN_2O^-/ArN_2^-), (Fig. 7), showes a linear dependence and the slope of 0.48 corresponds to reaction :

(IX) $$Ar-\overset{+}{N}\equiv N+2HO^- \rightleftarrows Ar-N=N-O^-+H_2O.$$

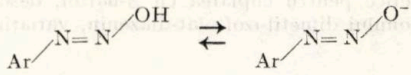
The equilibrium constant of the reaction (IX) is 7.8×10^{12}.

In the pH range of 7 ... 10, there are variations of absorbancy intensity at $\lambda_{max} = 260$ nm, correlated with a pseudo one order kinetics (Table 6).

The data of Table 6 show that the pseudo one order reaction constant increase in the pH range of 7 ... 9. In the pH range of 9 ... 10, there is a striking increase of the reaction rate constant, prooving the fact that the reaction does not follow a first order kinetics.

The first order kinetics holds in the pH range of 10 ... 14, absorbancy and reaction rate, being independent on pH.

At pH > 7, obtained by acidulation, a sudden decreasing of the absorbancy intensity takes place at the maximum corresponding to diazotate ($\lambda = 340$ nm), correlated with equilibrium reaction :



The absorbancy decreasing for subsequent acidulation is slow and finally, diazonium cation is formed.

Variation of absorbancy at $\lambda = 340$ nm, in the pH range of 1 ...8, led to obtention of the reaction rate constant values for a pseudo one order kinetics, presented in Table 7.

Table 7

Reaction of the Dimethyl Isophthalate Diazotate with Acid Solution at 20°C

pH	$k \times 10^3$, [s^{-1}]	pH	$k \times 10^3$, [s^{-1}]
1	5.5	5	2.5
2	3.0	6	1.7
3	2.6	7	0.5
4	2.4	8	0.06

As it comes out from Table 7, in the pH range of 3 ... 5, the first order kinetics fit the data and in the pH range of 6 ... 8, the reaction rate is low.

The acid — base equilibrium are accompanied by the tautomerism and *cis — trans* isomerization equilibrium, that will be studied next.

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STUDII SPECTRALE ASUPRA REACTIVITĂŢII UNOR CATIONI ARIL—DIAZONIU

(Rezumat)

S-a studiat reactivitatea acidului 5-amino-izoftalic şi a 5-amino-izoftalatului de metil, în contextul aplicării lor drept componente diazotate în sinteze de azopigmenţi.

Caracteristicile spectrale ale derivaţilor aminici şi diazoniu au fost corelate cu diagramele moleculare, obţinute prin aplicarea metodei HMO.

S-au efectuat studii cinetice pentru cuplarea cu β-naftol, descompunerea termică şi echilibrele acido-bazice ale cationului dimetil-izoftalat-diazoniu, variaţiile concentraţiilor fiind urmărite spectro-fotometric.

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POLY(ETHYLENE TEREPHTHALATE) CHARACTERIZATION

V. FRACTIONATION OF POLY(ETHYLENE TEREPHTALATE) MODIFIED WITH DIMETHYLISOPHTHALATE *)

BY

C. V. UGLEA, EMIL MATEI and ADRIANA MIHĂESCU

1. Introduction

As result of dimethylisophthalate (DMI), dimethylterephthalate (DMT) and ethyleneglycol (EG) copolycondensation, some products are obtained which may be used with succes for fibres and special sheets production. It is known the dependence between physical-mechanical properties of modified poly(ethylene therephthalate) (PET) and DMI amount contained in the main chain of PET [1], [2]. The influence of isophthalic structures on the result of modified PET fractionation was less studied.

The aim of the present paper is to compare the tesult of PET modified with DMI fractionation and the selection of the best method of separation.

2. Experimental

2.1. Reagents and Products

a) PET industrial grade as wet chips.

b) DMT, DMI and EG of industrial grade suitable for fibre processing.

c) PET 7.5 and PET 25 copolyesters obtained in the laboratory [3], by DMT, DMI and EG copolycondensation. The figures gave the amount of DMI (calculated as % vs. DMT weight) used in the esterinterchange step of copolyester processing.

2.2. Methods

a) *Fractionation by Coacervate Extraction.* PET polyester and PET 7.5 and PET 25 copolyesters were fractionated by coacervate extraction. For the extraction mixtures of solvent—nonsolvent (S—NS) of variable composition were used. As solvent mixture phenol : tetrachloroethane (F : TCE) 3 : 2 (g/g) and as NS acetone technical grade were used. Details on the working method were given in a previous paper [4]. The characteristics of fractions and unfractionated samples are given in Table 1. Distribution curves of the molecular weight obtained by this method are given in Fig. 1.

*) Presented at the 2 nd National Congres of Chemistry, Bucharest, 1981.

b) *Fractionation by Turbidimetric Titration.* Determination of molecular weight distribution (MWD) of the samples by turbidimetric titration was carried out according to the method described by V a s i l e [5]. Curves obtained are given in Fig. 2.

Table 1

Characteristics of Fractions Separated by Coacervate Extraction

No.	PET			PET 7.5				PET 25			
	$[\eta]$ dl/g	M_n	COOH eq/g 10^6	$[\eta]$ dl/g	M_n	COOH eq/g 10^6	DMI %	$[\eta]$ dl/g	M_n	COOH eq/g 10^6	DMI %
1	0.22	4 700	20.0	0.11	2 200	31.0	3.8	0.20	4 500	25.0	17.3
2	0.44	11 300	27.0	0.28	7 400	31.9	5.0	0.42	13 500	25.2	16.2
3	0.48	12 600	19.0	0.48	13 300	22.7	4.4	0.45	15 100	23.3	21.0
4	0.51	13 500	34.0	0.51	14 900	32.7	4.9	0.51	16 900	23.8	20.0
5	0.52	13 600	25.0	0.56	16 700	22.6	5.2	0.52	18 000	23.2	21.0
6	0.55	14 700	30.0	0.58	17 400	23.5	9.3	0.56	20 000	21.9	25.0
7	0.64	17 800	29.8	0.64	19 700	21.4	8.9	0.59	21 000	30.0	29.2
8	0.64	18 400	29.9	0.80	27 500	28.7	8.2	0.61	21 800	33.9	29.0
9	0.74	21 800	28.7	0.87	29 500	31.3	9.6	0.63	22 400	34.0	35.0
10	0.79	23 700	29.1	—	—	—	—	0.72	30 000	35.2	33.1
11	0.80	25 000	27.0	—	—	—	—	—	—	—	—
IS*	0.64	18 000	38.0	0.58	17 200	32.7	6.9	0.54	19 000	32.5	24.2

*) IS — initial samples.

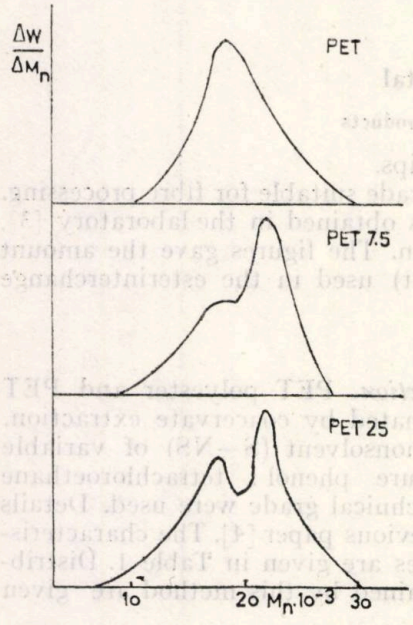

Fig. 1. — Distribution curves of molecular weight obtained by coacervate extraction.

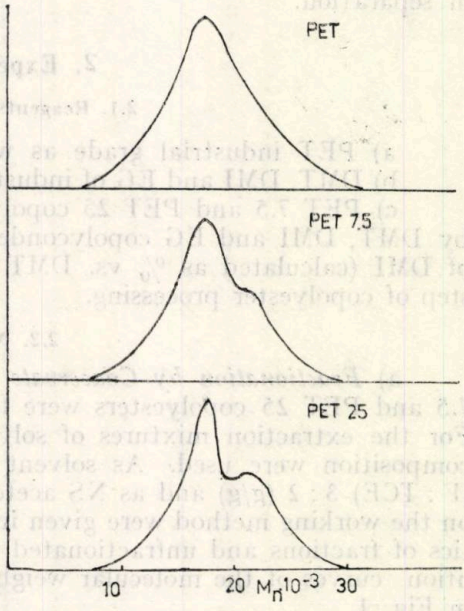

Fig. 2. — Distribution curves obtained by turbidimetric titration.

c) *Fractionation by Gel Permeable Chromatography* (GPC). Unfractionated polymers and some fractions separated by coacervate extraction were analysed by means of Waters Chromatograph Model 200. The samples were solved in F : TCE (3 : 2) and the elution was done by a mixture of TCE : nitrobenzene (95 : 5 v/v) at 100°C. Before use TCE was neutralised and stabilized as it follows : TCE fresh distillated was treated twice with a could aqueous solution of 5% K_2CO_3 (10 ml solution K_2CO_3/1 000 ml TCE) under stirring for 30 min. for each washing. After decantation of the aqueous phase 1 ml propilene oxide is added to 1 000 ml TCE ; then, TCE was mixed with nitrobenzene in the established ratio. The mixture was kept on silicagel till the use (10 g silicagel/1 000 ml mixture) in closed, brown bottles. These conditions for GPC fractionation were chosen to avoid the high viscosity of F : TCE mixture and the instability of PET solutions in TCE : nitrobenzene mixture. Gelchromatograms calibration (Fig. 3) was carried out by means of the universal method [6]. When the elution volumes V_{EL} of the samples were correlated with $\log[\eta]M$ it is not result a single curve valuable for all analysed samples but a „calibration surface" is obtained. This surface is limited by the curves corresponding to PET and PET 25 (Fig. 4). Data required for calibration were obtained

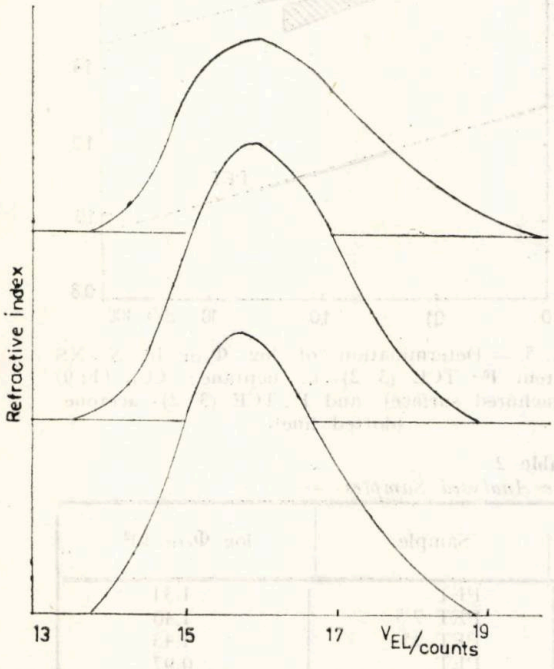

Fig. 3. — Gelchromatograms of analysed samples.

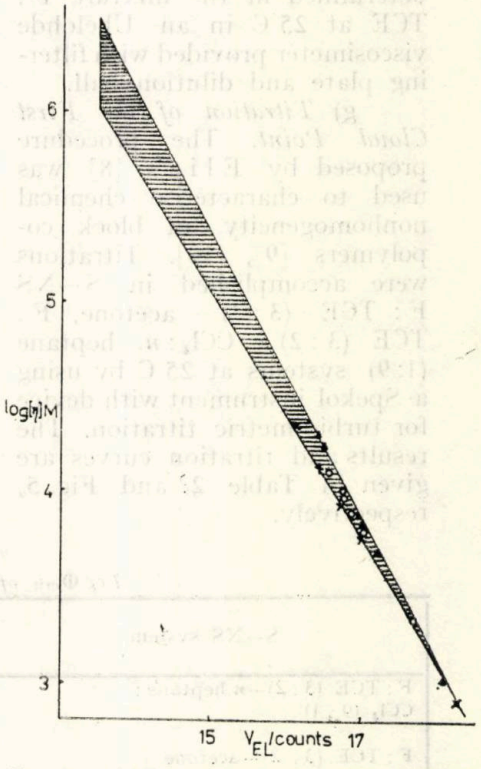

Fig. 4. — Calibration of gelchromatograms ×—PET ; o—PET 7.5 ; Δ—PET 25.

from Table 1 and from the gelchromatograms of the fractions separated by coacervate extraction. It should be pointed out that for these fractions unimodal gelchromatograms were obtained. The values of M_w/M_n ratios for the analysed samples by GPC were within 1.2 and 1.45. The above results allowed the conclusion that the fractionation by coacervate extraction showed a good efficiency.

d) *Determination of Molecular Weight.* Number average molecular weight (M_n) was determined by titration of the endgroups (method described by Conix [7] was applied). For unfractionated samples the weight average molecular weight (M_w) was also determined, in the experimental conditions depicted in [2]. Thus for M_w, the values 45 000, 44 500 and 47 900 were obtained which correspond to PET, PET 7.5 and PET 25, respectively.

e) *Determination of DMI Content.* Unfractionated samples and the fractions were saponificated with 1 N methanolic solution of KOH. The product was analysed by gaschromatography, diphenylether being used as internal standard.

f) *Intrinsic viscosity.* Flowing time of the solution was determined in the mixture F : TCE at 25°C in an Ubelohde viscosimeter provided with filtering plate and dilution ball.

g) *Titration of the First Cloud Point.* The procedure proposed by Elias [8] was used to characterise chemical nonhomogeneity in block copolymers [9], [10]. Titrations were accomplished in S—NS F : TCE (3 : 2) — acetone, F : TCE (3 : 2) — CCl_4 : *n.* heptane (1 : 9) systems at 25°C by using a Spekol instrument with device for turbidimetric titration. The results and titration curves are given in Table 2 and Fig. 5, respectively.

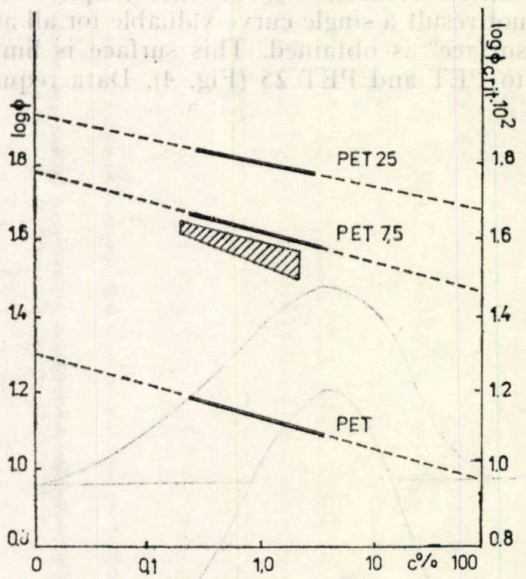

Fig. 5. — Determination of log Φ_{crit} in S—NS system F : TCE (3 : 2)—*n.* heptane : CCl_4 (1 : 9) (hachured surface) and F : TCE (3 : 2)—acetone (dotted line).

Table 2

Log Φ_{crit} of the Analysed Samples

S—NS system	Sample	log $\Phi_{crit} \cdot 10^2$
F : TCE (3 : 2)—*n.*heptane : CCl_4 (9 : 1)	PET	1.31
	PET 7.5	1.40
	PET 25	1.43
F : TCE (3 : 2)—acetone	PET	0.97
	PET 7.5	1.47
	PET 25	1.67

3. Discussion

From the Figs. 1 ... 3 could be drawn the conclusion that the shape and the position of the curves of MWD are dependent of the fractionating method and of S—NS system used to fractionate PET 7.5 and PET 25 samples.

Distribution curves of PET, obtained by the all three methods, are unimodal, the maximum corresponding to M_n =18 000.

Distribution curves of PET 7.5 and PET 25 samples, obtained by coacervate extraction, show a bimodal character, the position of the peaks corresponding to M_n =18 000 and 21 000, respectively, the last value being the main maximum (Fig. 1).

Bimodal character of the distribution curves of PET 7.5 and PET 25 samples is kept in the case of turbidimetric titration, the main maximum corresponding to M_n =18 000.

Gelchromatograms are unimodal, the peak corresponding to V_{EL} = =15.75 counts (1 counts=5 ml).

We consider that the bimodal shape of distribution curves obtained by coacervate extraction and turbidimetric titration for PET 7.5 and PET 25 samples is a result of chemical nonhomogeneity created by the presence of isophtalic structures in the main chain of PET. This supposition is supported by the modification of chemical composition of the fractions separated by coacervate extraction (Table 1). The separation process based on the dependence between the solubility and molecular weight is influenced, among others, by the composition or chemical structure of the species. One of the results of this influence is the distortion of distribution curves, process which can be reflected either by asymmetry or by bimodal character of these curves [10], [11]. We noticed that by including isophtalic structures in the main chain of PET, the polymer solubility is changed as result of supramolecular order disturbing. The increase of PET solubility due to DMI modification and its dependence on S—NS system is proved by the values of log Φ_{crit} determined by titration of the first cloud point (Fig. 5).

The results of coacervate extraction obtained in S—NS F : TCE (3 : 2) — acetone system are strongly influenced by chemical nonhomogeneity of the analysed samples. In this S—NS system species repartition between the two phases during coacervate extraction is also influenced by macromolecules chemical composition. Thus the different values of log Φ_{crit} and the the dominant bimodal character of distribution curves for PET 7.5 and PET 25 are explained. In the case of coacervate extraction the influence of sample chemical nonhomogeneity modifies so much the fractionation results that the main peak is drifted from M_n =18 000 to M_n =22 000.

Distribution curves determined by turbidimetric titration may also sustaines the dependence of fractionation results on experimental conditions of the separation. For S—NS F : TCE (3 : 2) — *n*. heptan : CCl_4(9 : 1) system, log Φ_{crit} is less dependent on DMI content from the analysed samples (points determined by titration of the first cloud point at the three analysed samples were spread in the hachured range in Fig. 5). The weaker bimodal

character of the distribution curves determined by turbidimetric titration is explained by the diminished sensibility of S—NS system towards DMI content of analysed samples.

When the results obtained by PET, PET 7.5 and PET 25 fractionating are compared it may be said that GPC is the best method recommended to be used to determine MWD in nonhomogeneous chemical polymers. But the analyse of the calibration surface given in Fig. 4 and the distribution curves from Fig. 3 show that GPC is influenced by the chemical nonhomogeneity too. The increase of $[\eta]M$ product is noticed during calibration as result of PET modification with DMI. This influence increases for higher values of molecular weight as it shown by hachured surface in Fig. 4. Gelchromatogram of PET 25 sample shows a marked asymmetry toward the range of low molecular weight species. A quantitative interpretation of the influence of chemical nonhomogeneity upon GPC results could be not obtained from these data. By correlating our data with those from [12] the total calibration surface could be determined.

4. Conclusions

Fractionation results for PET modified with DMI are dependent of experimental conditions. The influence on PET solubility of content in DMI is evidenced by titration of first cloud point.

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CARACTERIZAREA POLI(ETILEN TEREFTALATULUI)

V. Fracţionarea poli(etilen tereftalatului) modificat cu dimetilizoftalat

(Rezumat)

Se prezintă rezultatele obţinute la fracţionarea poli(etilen tereftalatului) modificat cu dimetilizoftalat. S-a evidenţiat influenţa sistematică a conţinutului de structuri izoftalice asupra formei şi poziţiei curbelor de distribuţie a maselor moleculare. Prin titrarea primului punct de precipitare s-a arătat influenţa conţinutului de DMI asupra solubilităţii poli(etilen tereftalatului).

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Secţia II
CHIMIE ŞI INGINERIE CHIMICĂ

ORTANSA PETROVANU

1931 — 1985

În ziua de 15 decembrie 1985 a încetat din viaţă în mod fulgerător conferenţiar doctor Ortansa Petrovanu, cadru didactic de elită a facultăţii de tehnologie chimică a Institutului politehnic din Iaşi.

Ortansa Petrovanu s-a născut la 30 ianuarie 1931 în oraşul Ploieşti, fiind cea de a patra fiică a familiei Minculescu.

În familie a primit o educaţie aleasă, care avea să se reflecte în comportarea ei de înaltă ţinută, ce a caracterizat-o şi prin care s-a impus.

Studiile medii şi le-a făcut în oraşul Ploieşti, iar în perioada 1950—1954 a urmat cursurile facultăţii de Chimie a Universităţii ieşene.

Activitatea în învăţământul superior a început-o la 21 februarie 1955 în calitate de preparator principal pe lîngă catedra de chimie organică a Universităţii din Iaşi, catedră condusă de profesorul C. V. Ghiorghiu (1894—1956). Sub îndrumarea acestui distins profesor şi-a început activitatea didactică şi de cercetare, reuşind ca numai peste un an să publice prima lucrare ştiinţifică

În anul 1971 şi-a susţinut cu mult succes teza de doctorat, avînd ca temă obţinerea unor N-metilolimide şi punerea în evidenţă a relaţiei dintre structura şi proprietăţile acestora, lucrare elaborată sub îndrumarea profesorului Ioan Zugrăvescu.

A urcat principalele trepte ale ierarhiei didactice, pînă la gradul de conferenţiar, pe care l-a ocupat prin concurs, în anul 1973, la disciplina de chimie, în cadrul I.C.P.P.D., Iaşi.

Activitatea sa didactică, desfăşurată pe parcursul a peste trei decenii, se caracterizează printr-un înalt grad de competenţă şi dăruire.

A lucrat pe lîngă disciplinele de chimie organică, chimie tehnologică, chimie generală, sinteze organice, metodica predării chimiei, aceasta din urmă fiind disciplina pe care a profesat-o şi în calitate de cadru didactic de predare, începînd cu anul 1965 pînă în 1973, cînd a început activitatea în cadrul Institutului de perfecţionare a cadrelor didactice din învăţământul mediu.

În cadrul acestui institut şi-a adus o contribuţie însemnată privind organizarea cursurilor de perfecţionare în conformitate cu necesităţile învăţământului preuniversitar, organizarea şi conducerea unor dezbateri metodice, întocmirea unor lecţii şi materiale didactice, elaborarea şi litografierea unor lucrări de ansamblu, necesare pregătirii cadrelor didactice.

A ţinut un număr mare de conferinţe şi lecţii metodice în toate oraşele mari ale Moldovei, contribuind în mod substanţial la informarea cadrelor didactice şi la orientarea activităţii acestora. A condus un număr mare de lucrări pentru acordarea gradului I profesorilor din Moldova.

În ultimii ani de activitate a depus o muncă susţinută, elaborînd două cărţi tipărite pe plan central prin Editura Didactică şi Pedagogică (1982 şi 1983), punînd astfel la dispoziţie profesorilor din întreaga ţară posibilitatea informării în domeniul metodicii predării chimiei. În ultima lună de viaţă a predat pentru litografiere cursul de Metodica predării chimiei.

În anul 1979, prin decizie ministerială, Ortansa Petrovanu a trecut în cadrul facultății de tehnologie chimică a Institutului politehnic, Iași, fiindu-i încredințate disciplinele de *Metodica predării chimiei* și cursul de *Chimie* pentru studenții facultății de mecanică. Concomitent s-a ocupat, în continuare, și de perfecționarea cadrelor didactice din învățămîntul preuniversitar.

Activitatea de cercetare științifică a conferențiarei Ortansa Petrovanu a fost orientată în domeniul sintezei organice. A sintetizat un număr mare de noi produși chimici, unii dintre ei avînd activitate biologică importantă. A pus în evidență activitatea fiziologică și proprietățile anticonvulsivante ale unei clase de compuși cu structură diacil-metilendiaminică. Și-a adus contribuția la rezolvarea multor cercetări pe bază de contract, cu diverse întreprinderi.

S-a afirmat pe plan național ca un specialist de autoritate în domeniul metodologiei predării chimiei, fiind unanim apreciată pentru competența pe care o demonstrase.

Ortansa Petrovanu avea față de toți colegii și față de studenți o comportare frumoasă, plină de înțelegere, caracterizată totdeauna de o ținută de înaltă demnitate. Purta o grijă nemărginită pentru familia ei și rămîne pentru toți cei care au cunoscut-o ca un exemplu de soție și mamă.

Încetarea prematură din viață, la numai cîteva ore de la terminarea activității didactice, a constituit o „lovitură de trăsnet", pentru toți care au cunoscut-o și apreciat-o.

Prin figura ei luminoasă, plină de bunătate și de omenie, cît și prin activitatea didactică și științifică desfășurată pînă în ultimile ore ale vieții sale, Ortansa Petrovanu rămîne un exemplu de cadru didactic căruia îi vom păstra o respectuoasă amintire.

Prof. dr. ing. S. Ifrim

I. P. Iaşi cd. 9

Puternicul colectiv de ingineri și tehnicieni de la Combinatul de Fibre Sintetice Săvinești, printr-o intensă muncă de cercetare aplicativă a elaborat și brevetat în numeroase țări tehnologii noi ca :

— Tehnologia de obținere a fibrelor acrilice sub forma de cablu, puf, pale.
— Prelucrarea fibrelor acrilice în fire pentru tricotaje.
— Tehnologia pentru vopsire în masă a fibrelor acrilice cu coloranți cationici.
— Tehnologia de obținere a fibrelor modacrilice.
— Tehnologia de obținere a firelor texturate covor din poliamida 6.
— Tehnologia de obținere a granulelor pe bază de poliamida 6 cu ingredienți.
— Tehnologia de polimerizare în bloc a caprolactamei (obținere de bare și plăci).
— Tehnologia de fabricare a acidului adipic din fenol și valorificarea acizilor bibazici secundari din soluțiile mume.

Aplicarea acestor tehnologii în producție a condus la :

— diversificarea gamei sortimentale ;
— dezvoltarea unor sortimente de fire și fibre poliamidice și poliacrilonitrilice cu proprietăți specifice domeniilor de utilizare ;
— reducerea costurilor de fabricație ;
— creșterea productivității muncii ;
— reducerea concentrației de noxe din apele reziduale.

Les ingénieurs et les techniciens du Combinat des Fibres Synthétiques de Săvineşti, par un intense travail de recherche appliquée, a élaboré et breveté dans des nombreux pays de nouvelles technologies, comme per exemple :

— La technologie pour l'obtention des fibres acryliques (câbles, poils).
— L'usinage des fibres acryliques en fils pour tricotages.
— La technologie pour teindre en masse les fibres acryliques avec décolorants cationiques.
— La technologie pour l'obtention des fibres modacryliques.
— La technologie pour l'obtention des fils texturés tapis de la polyamide 6.
— La technologie pour l'obtention des granules à base de polyamide 6 avec des ingrédients.
— La technologie de polymérisation en masse de la caprolactame (obtention des barres et des plaques).
— La technologie de fabrication de l'acide adipique en partant du phénol et la valorification des acides dibasiques secondaires des solutions-mère.

L'application de ces technologies a conduit à :

— la variété de la gamme des produits ;
— le développement des assortiments des fils et fibres polyamidiques et nitrile polyacryliques ayant des propriétés spécifiques pour les domaines d'utilisation ;
— la réduction des coûts de fabrication ;
— l'augmentation de la productivité du travail ;
— la réduction de la pollution des eaux résiduelles.

The team of engineers and technicians from Synthetic Fibres Works — Săvinești, after an intense research work have proposed and patented in numerous countries new technologies, namely :

— Technology for obtaining acrylic fibers (strand cable, fluf and top).
— Technology of processing acrylic fibers in filament yarn for knitting (textile yarn).
— Technology for blok dyeing of acrylic fibers with cationic dyes.
— Technology for obtaining modacrylic fibers.
— Technology for obtaining filament yarn texturized for carpets based on nylon-6.
— Technology for obtaining polyamide-6 grains with ingredients.
— Technology for blok-polymerization of E-caprolactame (producing of bars and plates).
— Technology for fabrication of adipic acid from phenol and render profilable secondary bibasic acids from native solutions.

Application of these technologies have result in :

— diversification of assortments ;
— development of some polyamidic and polyacrylonitrile assortments of fibers and yarns with specific properties ;
— reduction of fabrication costs ;
— rise of labour productivity ;
— reduction of harmfull staff water castes.

Das leistungsfähige Ingenieur- und Technikerkollektiv des Chemiefaserkombinates Săvineşti (Sozialistische Republik Rumänien) hat neue Technologien entwickelt und in zahlreichen Ländern patentiert, wie z. B. :

— Technologie zum Erhalt von Acrylfasern als Seil, Flaum und Lagen.
— Verarbeitung der Acrylfasern zu Fäden für Trikotagen.
— Technologie zum Massenfärben von Acrylfasern mit kationischen Farbstoffen.
— Technologie zum Erhalt von Modacrylfasern.
— Technologie zum Erhalt von Teppichfasern aus 6-Polyamid.
— Tehnologie zum Erhalt von Granulaten auf der Grundlage von 6-Polyamid mit Zusätzen.
— Blockpolymerisation von Kaprolaktam (Erhalt von Stangen und Platten).
— Technologie zur Produktion von Adipinsäure aus Phenol und durch Verwertung der sekundären bibasischen Säuren aus den Mutterlösungen.

Die Anwendung dieser Technologien in der industriemäßigen Produktion führte zur :

— Diversifikation der Sortimentenskala ;
— Entwicklung von Polyamid- und Pan-Faden- und Fasersortimenten mit spezifischen Eigenschaften entprechend dem Anwendungsgebiet ;
— Reduzierung der Produktionskosten ;
— Steigerung der Arbeitsproduktivität ;
— Reduzierung der Schadstoffkonzentration in den Abwässern.

térom(R)

SYNTHETIC FIBERS WORKS from Iași, a modern unit of advanced technology, much ahead in Romanian chemical industry, produces and delivers a wide range of polyester fibers, yarns and sheets, as well as equipments and spare parts for chemical and textile industry as the

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   - polyester fiber flax type ;
   - polyester fiber high shrinkage.
2. POLYESTER SYNTHETIC TEXTILE YARNS :
   - polyester continuous filament textile twisted yarns for curtains and tissues ;
   - polyester continuous filament drawn yarns for sewing thread ;
   - polyester continuous filament textured yarn (semi-dull or bright, round or profiles, raw white or dyed) for knittings, tissues or cloths.

Colour card for dyed yarns includes about 100 shades classified in : light, medium and heavy shades.

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— I.C.E. ELECTROEXPORTIMPORT Bucharest service 44 telex 11 388 for polyester sheets.

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